

# Vibrational Analysis of Water Using the SPC Force Field Model

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## Abstract

This study presents a computational vibrational analysis of water molecules using Simple Point Charge (SPC) force field model variants (SPC/E and SPC/FW). We developed a C++ program to simulate the atomic system of a water molecule, compute intramolecular and intermolecular energies, and derive forces to calculate the Hessian matrix via central difference approximations. Vibrational modes were obtained by diagonalizing the mass-weighted Hessian, yielding wavelength frequencies.

## 1 INTRODUCTION

Despite its simple molecular structure, water exhibits complex and unique properties that make it essential to life and has numerous scientific applications. This project investigates water’s vibrational properties by combining Simple Point Charge (SPC) water models with computational vibrational analysis techniques. By applying molecular mechanics and finite-difference methods to calculate mass-weighted Hessians, we derive vibrational frequencies that can be directly compared with experimental infrared spectroscopy data.

### 1.1 Background

#### 1.1.1 Simple Point Charge Model

The SPC model, introduced by Berendsen et al. in 1981, approximates water using fixed partial charges and a simplified potential energy to reproduce structural and thermodynamic properties [1]. The Extended Simple Point Charge (SPC/E) variant includes a correction for polarization energy [2], while the Flexible Simple Point Charge water (SPC/FW) model utilizes flexibility by modeling bond lengths and angles with harmonic force fields [3]. These models are widely used in classical molecular dynamics and allow water simulations.

#### 1.1.2 Parameters

The SPC model uses a three-site rigid representation of the water molecule with fixed geometry. In the SPC/E model, each water molecule consists of an oxygen atom and two hydrogen atoms arranged in a fixed bond angle of  $109.47^\circ$  and O-H bond length of  $1.0\text{\AA}$  [1]. The force field includes Lennard-Jones (LJ) interactions between oxygen atoms and Coulombic interactions between partial charges located on each atom (see Tables 2 and 1). The SPC/FW model extends SPC/E by allowing bond stretching and angle bending, parameterized by force constants for bond and angle terms [3].

#### 1.1.3 Infrared Spectroscopy

Infrared (IR) spectroscopy is a tool used to investigate the vibrational modes of molecules by measuring their absorption of infrared radiation at certain frequencies. Each trough or peak in an IR spectrum indicates a vibrational transition, which means that the molecule is vibrating at one of its natural modes [4].

#### 1.1.4 Vibrational Modes

Vibrational analysis of a water molecule shows several normal modes that belong in three broad categories: stretching, bending and librational motions [?]. The symmetric and asymmetric O-H stretching

modes are typically observed in the high frequency region from 3600-3700cm<sup>-1</sup> [? ]. The H-O-H bending mode is typically found around 1600 cm<sup>-1</sup> [? ]. In systems with more than one water molecule, low-frequency vibrations, typically below 300 cm<sup>-1</sup>, can occur. These vibrations include intermolecular bending and librations, which reflect restricted rotational motions caused by interactions, such as hydrogen bonding [? ]. These modes are essential to vibrational analysis because they provide insights into the behavior of water-based molecular networks.

## 1.2 Motivation

Understanding water’s vibrational properties is crucial for fields ranging from chemistry to materials science. Water’s unique properties, including its high boiling point, surface tension, and role as a universal solvent, stem from its molecular structure and the resulting vibrational characteristics. The study of water vibrations provides insight into hydrogen bonding networks, solvation processes, and interactions with solutes, all critical for applications in biochemistry, atmospheric science, and industrial processes.

The computational approach to vibrational analysis offers advantages over experimental methods, allowing precise control over the molecular environment and systematic investigation of specific structural effects. Force field models, particularly the SPC variants, provide computationally efficient frameworks for studying water dynamics at the molecular level. By implementing numerical methods to calculate vibrational frequencies and normal modes, we can evaluate the accuracy of these models against experimental spectroscopic data and gain a deeper understanding of the fundamental physics governing water behavior.

## 1.3 Objectives

The objective of this project was to compute and analyze the vibrational modes of water molecules using force field models. We began by constructing the atomic geometry from an input file, initializing each molecule with Cartesian coordinates in Bohr units. We then implemented the SPC/E model to evaluate the system’s total energy and force contributions, including Lennard-Jones interactions between oxygen atoms and Coulombic interactions between partial charges. From the forces, we then calculated the Hessian matrix using central finite differences. To prepare for vibrational analysis, we transformed the Hessian into mass-weighted coordinates. We then extended the model to SPC/FW, which allowed us to obtain eigenvalues and eigenvectors by diagonalizing the mass-weighted hessian. These values then allowed us to obtain the vibrational frequencies. This framework allowed a detailed investigation of both intra- and intermolecular vibrational behavior in water systems.

# 2 Methodology

## 2.1 Simulation Setup

Our simulation begins by reading text files that list water molecule coordinates. Each file starts with the number of atoms, followed by molecules in O-H-H order. Due to the rigid SPC model’s constraints and the unique equilibrium bond lengths and angles across SPC force field variants, we manually defined coordinates for systems with 1, 3, 5, and 10 water molecules in Ångströms. These are converted to Bohr units in the code for consistency, as we adopted atomic units throughout the implementation.

## 2.2 Extended Simple Point Charge Model

The SPC model is a computationally efficient pair potential for molecular dynamics (MD) simulations of liquid water, particularly for hydrated proteins [1]. It represents water as a rigid three-site molecule with point charges on the oxygen (-0.82 e) and two hydrogen atoms (+0.41 e each), forming an isosceles triangle with an O-H bond length of 1.0 Å and an H-O-H angle of 109.47°, ensuring charge neutrality. Intermolecular interactions include a Lennard-Jones (LJ) 6-12 potential between oxygen atoms and Coulomb interactions among all charged sites, as described by:

$$E_{SPC} = \sum_{i,j} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{R_{ij}} \right)^6 \right] + \frac{q_i q_j}{R_{ij}} \right\} \quad (1)$$

The SPC model was refined into the SPC/E model in 1987, which adjusts charges to account for polarization, improving predictions of water’s physical properties [2].

## 2.3 Flexible Water Simple Point Charge Model

The SPC/FW model was introduced in 2005 by Wu, Tepper and Voth. This model is an extension of the SPC and SPC/E models and adds intramolecular flexibility using harmonic potentials to regulate bond stretching and angle bending. This flexibility allows the model to more accurately capture vibrational properties and dynamic behaviors of water molecules. This makes the SPC/FW model useful for simulations that require vibrational analysis [3].

The total potential energy in the SPC/FW model consists of two components: intramolecular and intermolecular. Intramolecular energy accounts for the flexibility of the water molecule using harmonic potentials for bond stretching and angle bending:

$$E_{\text{intra}} = \sum_{\text{bonds}} \frac{1}{2} k_r (r - r_0)^2 + \sum_{\text{angles}} \frac{1}{2} k_\theta (\theta - \theta_0)^2$$

In this equation,  $k_r$  and  $k_\theta$  are force constants for bond and angle interactions, while  $r_0$  and  $\theta_0$  are the equilibrium bond length and bond angle (see Table 2). This allows for the energy to vary as the molecule deforms.

Intermolecular energy is calculated using a Lennard Jones potential and Coulombic interactions between all atomic sites.

$$V_{\text{inter}} = \sum_{i,j}^{\text{all pairs}} \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{R_{ij}} \right)^6 \right] + \frac{q_i q_j}{R_{ij}} \right\} \quad (2)$$

This equation describes non-bonded interactions between atoms  $i$  and  $j$ , where  $\epsilon_{ij}$  and  $\sigma_{ij}$  are Lennard-Jones parameters,  $q_i$  and  $q_j$  are partial charges, and  $R_{ij}$  is the distance between them.

By incorporating intramolecular flexibility, SPC/FW enables the evaluation of vibrational modes using the mass-weighted Hessian and normal mode analysis.

## 2.4 Energy

### 2.4.1 Coulombic Interactions

Electrostatic interactions play a critical role in both SPC/E and SPC/FW water models by accounting for long-range Coulomb forces between partial atomic charges. These interactions capture dipole-dipole alignment and hydrogen bonding effects, significantly impacting vibrational and structural behavior in simulations [9]. Each water molecule in both SPC/E and SPC/FW assigns fixed partial charges: for the oxygen atom and for each hydrogen [2]. These charges interact through the classical Coulomb potential:

$$E_{\text{Coulomb}} = \sum_{i,j} \frac{q_i q_j}{R_{ij}} \quad (3)$$

where  $q_i$  and  $q_j$  are the charges on atoms  $i$  and  $j$  and  $R_{ij}$  is the interatomic distance in Bohr. In our implementation, all non-bonded atom pairs are included in the summation, and the calculation is performed in vacuum without periodic boundary conditions. For SPC/E, all Coulomb interactions between distinct atom pairs are included since the model is rigid and does not separate intra- from intermolecular terms. However, for SPC/FW, Coulomb interactions are limited to intermolecular pairs. This exclusion avoids double counting short-range electrostatics already captured by the intramolecular harmonic bond and angle potentials [3].

### 2.4.2 Lennard-Jones Potential

The Lennard-Jones (LJ) potential models van der Waals interactions between non-bonded atoms, capturing both attraction at intermediate distances and repulsion at short ranges [9]. In the SPC water models, this potential is applied exclusively between oxygen atoms and is given by:

$$E_{\text{LJ}}(R) = \sum_{i,j} 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{R_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{R_{ij}} \right)^6 \right] \quad (4)$$

where  $\sigma_{OO}$  is the collision parameter,  $\epsilon_{OO}$  is the potential well depth, and  $R_{ij}$  is the interatomic distance. The  $R^{-12}$  term represents repulsion due to electron cloud overlap, while the  $R^{-6}$  term models attraction from induced dipole interactions [9].

The SPC/E model uses parameters  $\sigma_{OO} = 3.166 \text{ \AA}$  (5.982 Bohr) and  $\epsilon_{OO} = 0.650 \text{ kJ}\cdot\text{mol}^{-1}$  (0.000247 Hartree), while SPC/FW employs slightly adjusted values (see Table 2). Our implementation computes the LJ potential using a two-step approach where the  $r^{-6}$  term is calculated first, then squared to efficiently obtain the  $r^{-12}$  term. A cutoff distance of 18.90 Bohr limits the interaction range for computational efficiency.

### 2.4.3 Bond Energy

The SPC/E model assumes a rigid water molecule, therefore bond energy is not included in the calculations for that model. However, in the SPC/FW implementation, bond stretching is modeled using a harmonic potential applied to each O-H pair within a water molecule [3]. The energy contribution is given by:

$$E_{\text{bond}} = \frac{1}{2} k_r (r - r_0)^2, \quad (5)$$

where  $k_r = 0.474 \text{ Hartree/Bohr}^2$  is the bond force constant and  $l_0 = 1.912 \text{ Bohr}$  equilibrium O-H bond length.

This allows the simulation of vibrational modes involving bond stretching, which are inaccessible in rigid models like SPC/E. The energy is computed for both O-H bonds in each molecule and contributes to the total potential energy and vibrational spectrum. Bond flexibility improves agreement with experimental O-H stretching frequencies and captures the dynamic behavior of liquid water [10]. For specific bond lengths  $r_{OH}$  see Table 1 for SPC/E and Table 2 for SPC/FW.

### 2.4.4 Angle Energy

The SPC/E model assumes a rigid water molecule, so intramolecular angle energy is not explicitly calculated in our implementation [2]. However, the SPC/Fw model includes a harmonic angle potential for the H-O-H angle to model vibrational flexibility [9]:

$$E_{\text{angle}} = \frac{1}{2} k_{\theta} (\theta - \theta_0)^2, \quad (6)$$

where  $k_{\theta} = 0.145 \text{ Hartree/rad}^2$  and  $\theta_0 = 113.24^\circ$  (1.976 radians) [9].

This harmonic approximation is accurate for small deviations ( $\pm 20^\circ$ ) from the equilibrium angle in water, but may require higher-order terms (e.g., cubic) for larger deformations, especially since oxygen is a divalent atom where an H-O-H angle of  $180^\circ$  is an energy maximum [9]. However, the harmonic term is sufficient for most applications, as angle deviations typically remain small (within 40 kJ/mol above the minimum) [9]. In our SPC/E implementation, the fixed HOH angle of  $109.47^\circ$  is maintained implicitly through the input geometry, and no angle energy term is computed [2].

## 3 Normal Mode Analysis

### 3.1 Forces

In our simulation, forces on each atom are calculated using the central difference method, a numerical approximation of the potential energy gradient. For each atomic coordinate  $x_i$ , the force  $F_i$  is approximated as  $F_i \approx -\frac{E(x_i+h) - E(x_i-h)}{2h}$ , where  $E$  is the total potential energy from the SPC/E and SPC/FW water models and  $h = 0.01890 \text{ Bohr}$  for displacement step size. This method provides second-order accuracy in approximating derivatives while avoiding the need for analytical force expressions. The implementation systematically displaces each atom in each coordinate direction, computes the total energy for these displaced configurations, and applies the central difference formula to obtain force components. For

every atom and coordinate pair, we create two configurations with positive and negative displacements, evaluate the SPC energy function for each, and derive the corresponding force component from the energy difference. The resulting forces are organized in a  $3 \times N$  matrix, where each column represents the three-dimensional force vector acting on a specific atom. These calculated forces serve dual purposes: they provide insight into the equilibrium state of the system (where forces should approach zero) and they constitute essential inputs for the subsequent Hessian matrix computation, which requires force evaluations at displaced geometries.

### 3.2 Hessian Matrix

The Hessian matrix represents the second derivatives of energy with respect to atomic displacements, serving as the cornerstone of vibrational analysis. In mathematical terms, each element is defined as  $H_{ij} = \frac{\partial^2 E}{\partial x_i \partial x_j}$ , or equivalently, in terms of force gradients as  $H_{ij} = -\frac{\partial F_i}{\partial x_j}$ . This matrix  $3N \times 3N$  (where  $N$  is the number of atoms) contains complete information about the local curvature of the potential energy surface, determining the vibrational modes and their frequencies. We compute Hessian numerically using a second-order central difference method, approximating each element as  $H_{ij} \approx -\frac{F_i(x_j+h) - F_i(x_j-h)}{2h}$ , where  $F_i(x_j+h)$  represents the  $i$ -th force component when the  $j$ -th coordinate is displaced by  $h$ . Our algorithm systematically processes each atomic coordinate, creating displaced configurations, calculating complete force sets for each displacement, and applying the central difference formula to derive Hessian elements. We use a step size of  $h = 0.007559$  Bohr, carefully chosen to balance precision and numerical stability. Although the Hessian is inherently symmetric due to the conservative nature of the force field, we explicitly enforce the symmetry condition  $H_{ij} = H_{ji}$  to mitigate numerical errors. A notable feature of our implementation is its hierarchical computation strategy: forces at displaced positions are themselves calculated using central differences, resulting in a nested differentiation scheme that effectively computes second derivatives through the sequential application of first-derivative approximations.

#### 3.2.1 Mass-Weighting

To compute vibrational frequencies from the Hessian Matrix, it must be transformed into mass-weighting coordinates. Because each atom has a different mass, the unweighted eigenvalues do not directly correspond to vibrational frequencies. The mass-weighted Hessian  $\mathbf{H}_m$  is calculated by dividing each element of  $\mathbf{H}$  by the square root of the product of the atomic masses associated with the corresponding coordinates:

$$H_{m,ij} = \frac{H_{ij}}{\sqrt{m_i m_j}}, \quad (7)$$

Here,  $m_i$  and  $m_j$  are the atomic masses for the degrees of freedom  $i$  and  $j$ , respectively. Atomic masses employed are 16.00 amu for oxygen and 1.008 amu for hydrogen. This conversion serves to standardize atomic mass effects and ensure all vibrations occur on an equal basis mechanically [11].

#### 3.2.2 Diagonalization

After mass-weighting the Hessian, its eigenvalue is solved:

$$\mathbf{H}_m \mathbf{v} = \lambda \mathbf{v}, \quad (8)$$

where  $\lambda$  are the eigenvalues corresponding to squared vibrational frequencies (in atomic units), and  $\mathbf{v}$  are the eigenvectors representing the normal modes of vibration. The diagonalization is performed using a symmetric eigensolver to yield a complete set of vibrational modes [11].

To convert the eigenvalues to frequencies in wavenumbers ( $\text{cm}^{-1}$ ), the conversion factor is applied:

$$\tilde{\nu} = \sqrt{\lambda} \times C, \quad (9)$$

where  $C = 5140.484532 \text{ cm}^{-1}$  is the conversion factor from atomic units [? ]. Positive eigenvalues are associated with vibrational frequencies, whereas negative eigenvalues indicate imaginary frequencies, which may be associated with non-equilibrium geometries or numerical noise. Additionally, non-zero values that may result due to numerical error are discarded from the analysis [11].

## 4 Results and Discussion

### 4.1 Vibrational Analysis

#### 4.1.1 Mode Classification

For a non-linear molecule like water, the total number of degrees of freedom is  $3N = 9$ , where  $N = 3$  atoms. Of these, 3 correspond to translational motion and 3 to rotational motion, leaving 3 internal degrees of freedom, which are classified as vibrational modes [11].

These vibrational modes include:

- Symmetric O–H stretch
- Asymmetric O–H stretch
- H–O–H bending mode

In the case of a single, isolated water molecule, only these three vibrational modes are present. However, when multiple water molecules are simulated together—especially at intermolecular distances that enable hydrogen bonding—additional low-frequency modes appear.

These are known as librational modes, which correspond to hindered rotational motions caused by intermolecular interactions. Librations arise due to coupling between neighboring water molecules, especially through hydrogen bonding, and typically appear below  $300\text{ cm}^{-1}$  in the vibrational spectrum [12]. They are absent in single-molecule systems, but they become prominent in small clusters and bulk phases.

### 4.2 SPC/E

Our SPC/E water model simulations yielded vibrational frequencies from  $214\text{--}1510\text{ cm}^{-1}$ , with four modes clustered between  $1361\text{--}1510\text{ cm}^{-1}$  and one at  $214\text{ cm}^{-1}$ , Table 3. As Figure ?? shows, these calculated frequencies (red dashed lines) align with regions of the experimental IR spectrum.

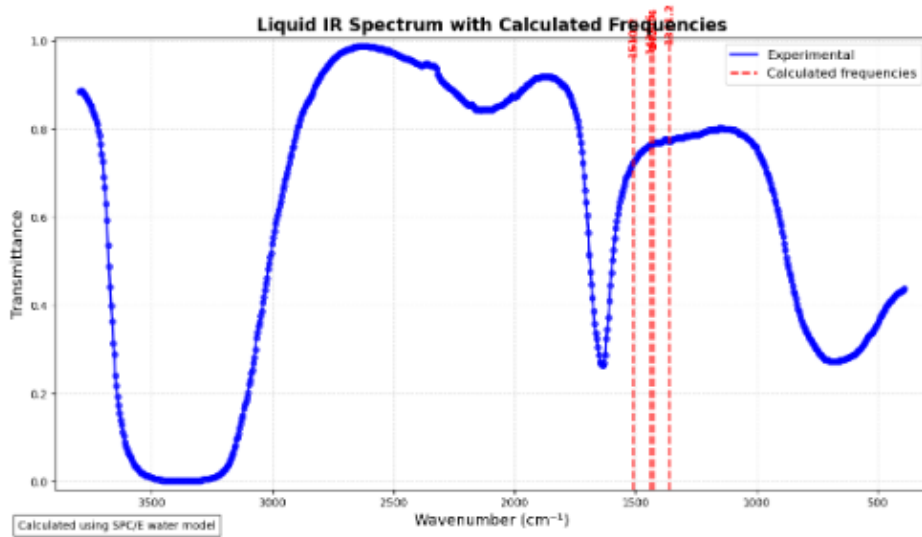


Figure 1: Liquid IR spectrum of an isolated water molecule. Experimental data (blue solid line) compared with SPC/E model-derived vibrational frequencies (red dashed lines) in the wavenumber region from  $500\text{--}4000\text{ cm}^{-1}$ .

Notably, despite being a rigid model without explicit angle potentials, SPC/E captures frequencies in the bending region ( $1361\text{--}1510\text{ cm}^{-1}$ ). This may result from atomic displacements altering H–O–H angles during Hessian calculation, creating Coulombic energy variations that function as effective bending force constants. However, the model fails to reproduce O–H stretching frequencies ( $3400\text{--}3600\text{ cm}^{-1}$ ) due to its rigid bond constraints.

Our analysis reveals a total energy of  $-0.32489$  Hartree, primarily from Coulombic interactions ( $-0.32290$  Hartree) with minor polarization contribution ( $-0.00199$  Hartree). The numerical Hessian calculation produced expected zero-frequency modes (with some numerical artifacts) consistent with a three-atom non-linear molecule.

While SPC/E adequately reproduces water’s bending region vibrations, its rigid framework limits its ability to represent the complete vibrational landscape, particularly in hydrogen-bonded systems.

### 4.3 SPC/FW

Simulations using the SPC/FW model yielded vibrational frequencies ranging from near 0 to  $3677\text{ cm}^{-1}$  for both isolated and clustered water molecules. For a single H<sub>2</sub>O molecule, as seen in Figure 2, stretching frequencies appear at 3592 and  $3677\text{ cm}^{-1}$ . This aligns well with the experimental values of  $3200\text{--}3650\text{ cm}^{-1}$  and validates the harmonic bond representation of the SPC/FW model. The bending mode is underestimated, with the frequency appearing at  $1502\text{ cm}^{-1}$ . This is about  $100\text{ cm}^{-1}$  below the experimental bending frequency of  $1600\text{ cm}^{-1}$ . This discrepancy may be due to an overly stiff angle force in the SPC/FW harmonic potential, which underestimates the restoring force and shifts the frequency downward [15].

Low-frequency modes at  $0.12$ ,  $53.22$ , and  $86.57\text{ cm}^{-1}$  are also present, but given that this is a single, isolated water molecule, these likely arise from numerical errors or residual translational and rotational motions rather than physical behavior [11].

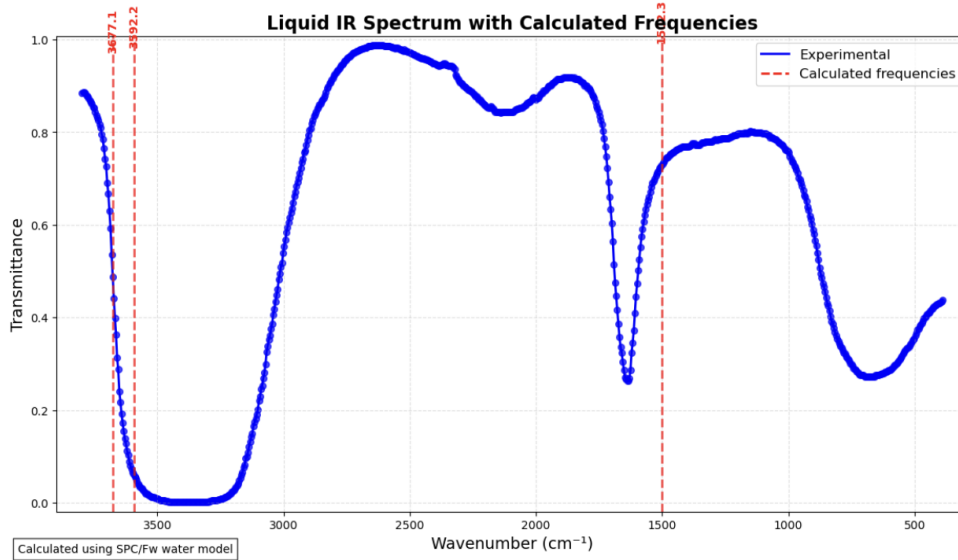


Figure 2: Liquid IR spectrum of an isolated water molecule. Experimental data (blue solid line) compared with SPC/Fw model-derived vibrational frequencies (red dashed lines) in the wavenumber region from  $500\text{--}4000\text{ cm}^{-1}$ . For exact values refer to Table 4

For the 3-molecule system, as seen in Figure 3, multiple low-frequency modes appear below  $300\text{ cm}^{-1}$  at  $84.78$ ,  $144.88$ , and  $203.18\text{ cm}^{-1}$ . These are not observed in the isolated case and probably represent intermolecular bending and restricted rotational motions (librations) resulting from weak dipole-dipole coupling or close interactions [13]. Although the separation of  $3\text{ \AA}$  is a slightly larger distance than classical hydrogen bond distances, the vibrational modes reflect partial collective motion among neighboring water molecules.

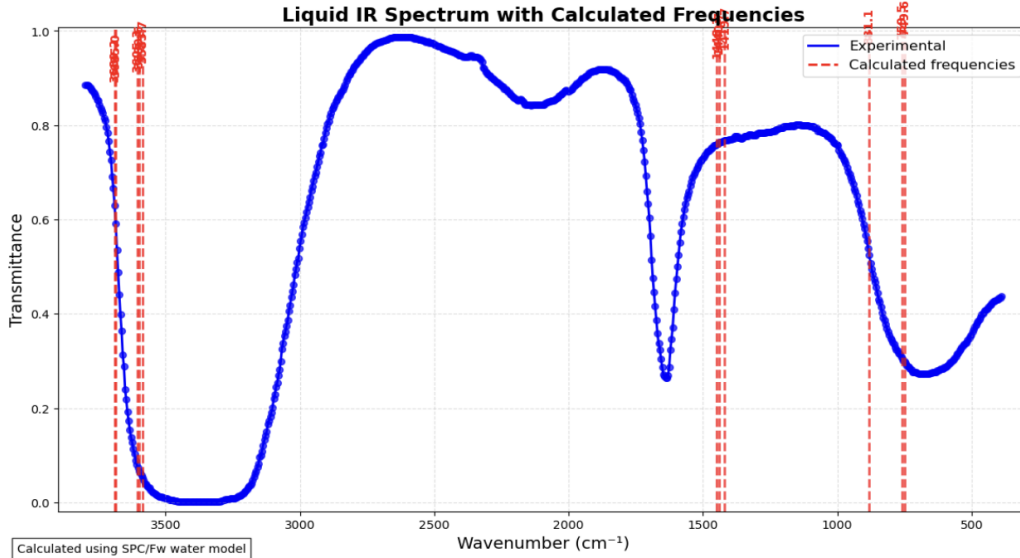


Figure 3: Liquid IR spectrum of three water molecules spaced  $3 \text{ \AA}$  apart. Experimental data (blue solid line) compared with SPC/Fw model-derived vibrational frequencies (red dashed lines) in the wavenumber region from  $500\text{--}4000 \text{ cm}^{-1}$ . For exact values refer to Table 4

Unlike SPC/E, the SPC/FW model reproduces both bending and stretching modes due to its inclusion of intramolecular bond and angle flexibility. The presence of low-frequency intermolecular modes further demonstrates the model’s capability for reproducing vibrational coupling effects, though it may underestimate the strength of these interactions compared to experiment due to the lack of polarizability or quantum corrections [15].

The bending modes in this system are spread across  $1419\text{--}1448 \text{ cm}^{-1}$ , still slightly underestimated. Meanwhile, the O–H stretching region remains consistent with experiment, spanning  $3585\text{--}3698 \text{ cm}^{-1}$ .

In summary, the SPC/FW model effectively reproduces stretching frequencies and captures additional low-frequency features. While it tends to underestimate bending frequencies, this behavior is expected due to its harmonic parameterization and the absence of polarizability.

#### 4.4 Hydrogen Bonding

To explore the effects of hydrogen bonding on vibrational frequencies, we compared two three-water systems using the SPC/FW model: one in which molecules are spaced  $5 \text{ \AA}$  apart, to minimize interactions, and another in which molecules are separated by  $2.2 \text{ \AA}$  to permit hydrogen bonding.



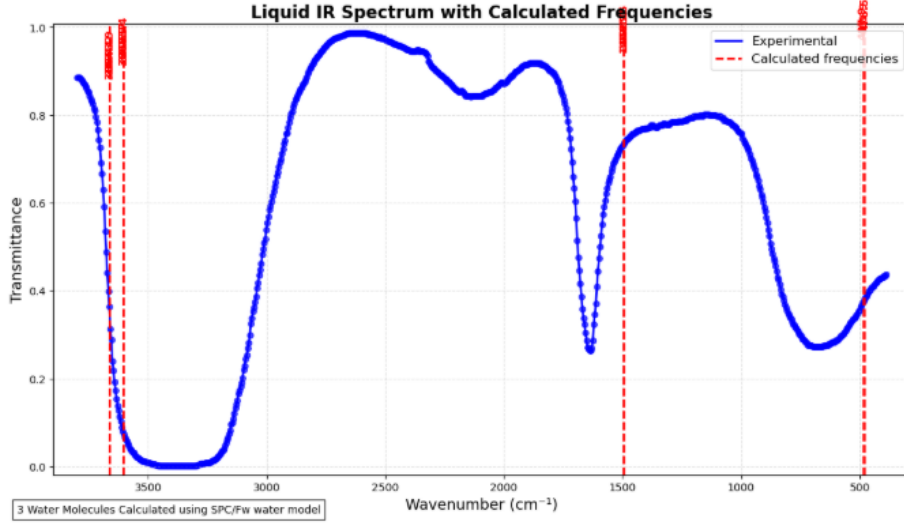


Figure 4: Liquid IR spectrum of three non-interacting water molecules spaced 5 Å apart. Experimental data (blue solid line) compared with SPC/Fw model-derived vibrational frequencies (red dashed lines) in the wavenumber region from 500–4000  $\text{cm}^{-1}$ . For exact values refer to Table 5.

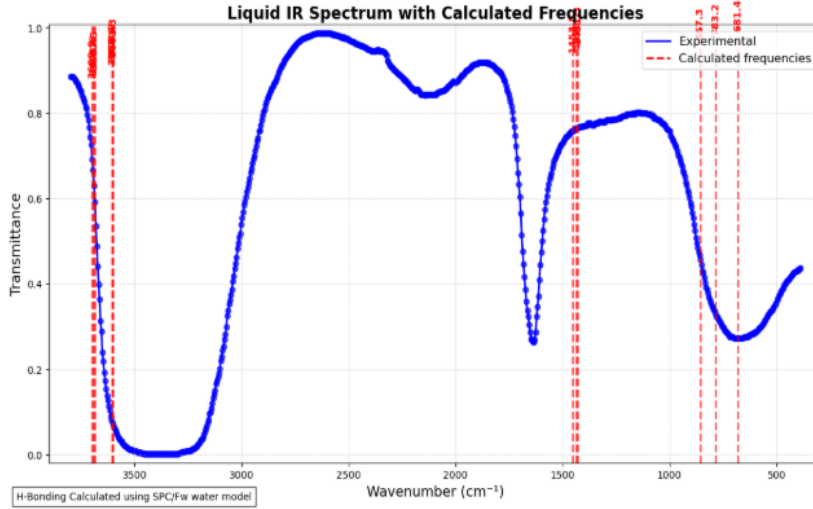


Figure 5: Liquid IR spectrum of three hydrogen-bonded water molecules spaced 2.2 Å apart. Experimental data (blue solid line) compared with SPC/Fw model-derived vibrational frequencies (red dashed lines) in the wavenumber region from 500–4000  $\text{cm}^{-1}$ . For exact values refer to Table 5.

In the O–H stretching region, as seen in Figure 5, the hydrogen-bonded system shows a red shift of 3–4  $\text{cm}^{-1}$  compared to the non-interacting system. This downshift is an indicator of hydrogen bonding, which weakens the O–H bond and lowers the vibrational frequency of the stretch [? ].

The H–O–H bending region also shows a clear downshift. For the 5 Å system, as seen in Figure 4, bending modes cluster around 1495–1497  $\text{cm}^{-1}$ , which closely matches the experimental bending frequency of 1600  $\text{cm}^{-1}$ . In contrast, the hydrogen-bonded system shows a shift to lower values between 1431–1453  $\text{cm}^{-1}$ , suggesting that intermolecular interactions from hydrogen bonding reduce the restoring force associated with the H–O–H angle.

The biggest difference appears in the low-frequency region. The hydrogen-bonded system contains significantly more modes below 300  $\text{cm}^{-1}$ , which are mostly absent in the 5 Å system. These new modes are attributed to intermolecular motions such as librations, bending and hindered translations, which

arise due to the restricted movement of water molecules that are engaged in hydrogen bonding.

Overall, hydrogen bonding leads to red shifts in O–H stretching and H–O–H bending modes and introduces new low-frequency vibrations. These shifts reflect weakened bonds and restricted motion from intermolecular interactions. While SPC/FW may show these effects, it underestimates their magnitude due to the lack of polarizability and quantum effects [15].

## 5 Conclusion

This study demonstrates the effectiveness of numerical vibrational analysis applied to SPC water models. The SPC/E model successfully reproduces bending modes ( $1361\text{--}1510\text{ cm}^{-1}$ ) but cannot capture O–H stretching vibrations due to its rigid framework. In contrast, the SPC/FW model effectively reproduces both stretching ( $3592\text{--}3677\text{ cm}^{-1}$ ) and bending modes ( $\sim 1500\text{ cm}^{-1}$ ) through its harmonic bond and angle potentials.

Our hydrogen bonding analysis revealed frequency red shifts and new low-frequency modes, confirming that SPC/FW qualitatively represents these intermolecular effects. The numerical central difference approach proved effective, balancing computational efficiency and accuracy for vibrational analysis.

This work contributes to understanding water’s vibrational properties through computational methods and provides a foundation for investigating more complex water-based systems, particularly those involving hydrogen bonding networks or proton transfer processes.

### 5.1 Future Works

#### 5.1.1 Computational Framework Enhancement

Future development will focus on creating a modular pipeline that accommodates multiple SPC variants without separate implementations, enabling rapid comparison between water models and supporting custom force field modifications.

#### 5.1.2 Zundel Cation Investigation

Applying our framework to the Zundel cation ( $\text{H}_5\text{O}_2^+$ ) would test the limits of classical models for representing proton transport phenomena. The characteristic proton shuttle mode at approximately  $1200\text{ cm}^{-1}$  could bridge the gap between computational efficiency and physical accuracy in simulating protonated water structures.

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## APPENDIX

Table 1: Parameters of the SPC/E Water Model

Parameter	Original Theoretical Values	Converted to Atomic Units
$\sigma_{OO}$	3.166 Å	5.982 Bohr
$\epsilon_{OO}$	0.650 kJ·mol <sup>-1</sup>	0.000247 Hartree
$r_{OH}$	1.000 Å	1.889 Bohr
$\angle HOH$	109.5 °	1.911 Radian
$q_O$	-0.8476 e	-0.8476 e
$q_H$	0.4238 e	0.4238 e
Polarization Constant	1.25 kcal·mol <sup>-1</sup>	-0.001992 Hartree

Table 2: Parameters of the SPC/FW Water Model

Parameter	Original Theoretical Values	Converted to Atomic Units
$\sigma_{OO}$	3.165 Å	5.982 Bohr
$\epsilon_{OO}$	0.1554 kcal·mol <sup>-1</sup>	0.000247 Hartree
$q_O$	-0.82 e	-0.82 e
$q_H$	0.41 e	0.41 e
$k_r$	1059 kcal·mol <sup>-1</sup> ·Å <sup>-2</sup>	0.474 Hartree/Bohr <sup>2</sup>
$r_{eq,OH}$	1.012 Å	1.912 Bohr
$k_\theta$	75.9 kcal·mol <sup>-1</sup> ·rad <sup>-2</sup>	0.145 Hartree/rad <sup>2</sup>
$\angle_{eq}HOH$	113.2 °	1.976 Radian

Table 3: SPC/E Results

Mode	Frequency (cm <sup>-1</sup> )
1-4	Imaginary
5	214.00
6	1361.22
7	1427.41
8	1438.61
9	1510.16

Table 4: Vibrational Frequency Analysis of 1 vs. 3 Water Molecules (SPC/Fw Model)

Mode	1 H <sub>2</sub> O Molecule (cm <sup>-1</sup> )	3 H <sub>2</sub> O Molecules (cm <sup>-1</sup> )
1	Imaginary (-0.00034)	Imaginary (-0.07333)
2	Imaginary (-0.00000)	Imaginary (-0.07311)
3	Imaginary (-0.00000)	Imaginary (-0.06828)
4	0.12060	Imaginary (-0.00626)
5	53.22013	Imaginary (-0.00347)
6	86.56577	Imaginary (-0.00097)
7	1502.25602	Imaginary (-0.00019)
8	3592.24853	Imaginary (-0.00004)
9	3677.14667	Imaginary (-0.00002)
10	—	Imaginary (-0.00000)
11	—	0.00456
12	—	0.01218
13	—	84.78354
14	—	144.88435
15	—	203.18281
16	—	749.55308
17	—	759.53739
18	—	881.06060
19	—	1419.65401
20	—	1440.73534
21	—	1448.32118
22	—	3585.65498
23	—	3599.59959
24	—	3605.34397
25	—	3685.00090
26	—	3689.19799
27	—	3698.80347

Table 5: Hydrogen Bonding Analysis

Table 6: Comparison of Vibrational Modes for 3 H<sub>2</sub>O Molecules vs. Hydrogen-Bonded System

Mode	3 H <sub>2</sub> O Molecules (cm <sup>-1</sup> )	H-Bonded System (cm <sup>-1</sup> )
1-10	Imaginary	Imaginary
11	5.36	0.00514
12	10.73	0.00618
13	28.03	8.87
14	37.56	94.79
15	47.80	207.10
16	478.48	270.95
17	481.90	681.42
18	487.93	783.23
19	1495.52	857.31
20	1496.04	1431.32
21	1496.85	1435.15
22	3605.38	3601.30
23	3605.68	3603.87
24	3605.90	3605.55
25	3663.86	3687.49
26	3664.18	3691.61
27	3664.39	3699.93