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Absorption Spectra of Water Clusters Calculated Using Density Functional Theory

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14. ABSTRACT We present calculations of ground and excited state resonance structure associated with clusters of water molecules that are randomly distributed and in liquid-phase using density functional theory (DFT) and its extension, time-dependent density functional theory (TD-DFT). Calculation of ground and excited state resonance structure using DFT and TD-DFT can provide interpretation of absorption spectra with respect to molecular structure for excitation by electromagnetic waves at frequencies within the IR and UV ranges. The dielectric response of a molecular cluster consisting of a given number of molecules should be associated with response features that are intermediate between that of isolated molecules and that of a bulk lattice. The DFT software GAUSSIAN was used for the calculations of ground and excited state resonance structure presented here.					
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Introduction

The present study is based on significant progress in density functional theory (DFT), and associated software technology, which is sufficiently mature for the determination of dielectric response structure, and should actually provide complementary information to that obtained from experiment. Calculations are presented of ground and excited state resonance structure associated with clusters of water molecules that are randomly distributed and in liquid-phase using density functional theory (DFT) and its extension, time-dependent density functional theory (TD-DFT). Calculation of ground and excited state resonance structure using DFT and TD-DFT, respectively, can provide interpretation of absorption spectra with respect to molecular structure for excitation by electromagnetic waves at frequencies within the IR and UV ranges. The absorption spectrum of a molecular cluster consisting of a given number of water molecules should be associated with response features that are intermediate between that of isolated molecules and that of a bulk lattice. In principle, these absorption spectra should provide quantitative initial estimates of spectral response features that can be subsequently adjusted with respect to additional information such as laboratory measurements and other types of theory based calculations, or conversely, adapted as constraints for the inverse analysis of experimentally measured absorption spectra. A significant aspect of using DFT for the calculation of absorption spectra is that it adopts the perspective of computational physics, according to which a numerical simulation represents another source of “experimental” data.

Density functional theory has been successfully used to investigate the vibrational spectra of energetic materials in the form of single molecules and molecular crystals [1-9]. These calculations provide interpretation of absorption spectra with respect to molecular structure for various forms of materials, which can be encountered in various detection scenarios. In particular, the calculated absorption spectra of isolated molecules can help to identify intramolecular vibrational modes of various materials. A series of studies have focused on the general concept of constructing dielectric response functions using DFT for the purpose of quantitative simulation of explosives detection scenarios [9,10,11]. For these studies the DFT software GAUSSIAN09 (G09) was adopted [12]. As emphasized in these studies, the calculation of absorption spectra using DFT defines a general approach where dielectric response is estimated within the bounds of relatively well-defined adjustable parameters. Following this approach, permittivity functions are constructed using DFT calculated absorption spectra under the condition that the calculated resonance locations are fixed, while resonance widths and number densities are assumed adjustable with respect to additional information such as experimentally observed spectra or more advanced theory.

Previous studies have examined various properties of water molecules and their clusters [13-21]. The absorption spectrum of molecular clusters consisting of water molecules should be of significance for interpretation of absorption spectra associated with detection in practice. This follows in that most environments associated with detection in practice include the presence of water in one form or another. These forms can range from isolated molecules in gas phase, molecular clusters, adsorbed surface layers, droplets and interface regions in liquid phase, and ice. Absorption spectra of molecular clusters consisting of water represent a separate regime for dielectric response with respect to electromagnetic wave excitation. This regime should be better quantified for improved interpretation of absorption spectra associated with systems that include water clusters as components.

The organization of the subject areas presented are as follows. First, a general review of the elements of vibrational analysis using DFT that are relevant for the calculation of absorption spectra is presented. Second, calculations are presented of ground and excited state resonance structure of water clusters consisting of randomly-distributed molecules. Third, calculations are presented of ground and excited state resonance structure of liquid-phase water clusters. Fourth, calculations are presented of bond paths associated with equilibrium configurations of water clusters.

Calculation of Absorption Spectra using DFT

As in previous studies [9, 10, 11] the formal mathematical structure underlying DFT calculations, as well as the procedure for calculation of absorption spectra corresponding to vibrational states, is included here for purposes of completeness. The extension of DFT for the calculation of absorption spectra corresponding to electronic excitation states, which is the formalism of time-dependent density functional theory (TD-DFT), is described in reference [22].

The DFT software GAUSSIAN09 (G09) can be used to compute an approximation of the IR absorption spectrum of a molecule or molecules [23]. This program calculates vibrational frequencies by determining second derivatives of the energy with respect to the Cartesian nuclear coordinates, and then transforming to mass-weighted coordinates at a stationary point of the geometry. The IR absorption spectrum is obtained using density functional theory to compute the ground state electronic structure in the Born-Oppenheimer approximation using Kohn-Sham density functional theory [24-29]. GAUSSIAN uses specified orbital basis functions to describe the electronic wavefunctions and density. For a given set of nuclear positions, the calculation directly gives the electronic charge density of the molecule, the potential energy V , and the displacements in Cartesian coordinates of each atom. The procedure for vibrational analysis followed in GAUSSIAN is that described in Ref [23]. Reference [29] presents a fairly detailed review of this procedure. A brief description of this procedure is as follows.

The procedure followed by GAUSSIAN is based on the fact the vibrational spectrum depends on the Hessian matrix $\mathbf{f}_{\text{CART}}$, which is constructed using the second partial derivatives of the potential energy V with respect to displacements of the atoms in Cartesian coordinates. Accordingly, the elements of the $3N \times 3N$ matrix $\mathbf{f}_{\text{CART}}$ are given by

$$f_{\text{CART}ij} = \left(\frac{\partial^2 V}{\partial \xi_i \partial \xi_j} \right)_0 \quad (1)$$

where $\{\xi_1, \xi_2, \xi_3, \xi_4, \xi_5, \xi_6, \dots, \xi_{3N}\} = \{\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \dots, \Delta z_N\}$, which are displacements in Cartesian coordinates, and N is the number of atoms. As discussed above, the zero subscript in Eq.(1) indicates that the derivatives are taken at the equilibrium positions of the atoms, and that the first derivatives are zero. Given the Hessian matrix defined by Eq.(1) the operations for calculation of the vibrational spectrum require that the Hessian matrix Eq.(1) be transformed to mass-weighted Cartesian coordinates according to the relation

$$f_{\text{MWC}ij} = \frac{f_{\text{CART}ij}}{\sqrt{m_i m_j}} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 \quad (2)$$

where $\{q_1, q_2, q_3, q_4, q_5, q_6, \dots, q_{3N}\} = \{\sqrt{m_1} \Delta x_1, \sqrt{m_1} \Delta y_1, \sqrt{m_1} \Delta z_1, \sqrt{m_2} \Delta x_2, \sqrt{m_2} \Delta y_2, \sqrt{m_2} \Delta z_2, \dots, \sqrt{m_N} \Delta z_N\}$ are the mass-weighted Cartesian coordinates. GAUSSIAN computes the energy second derivatives Eq.(2), thus computing the forces for displacement perturbations of each atom along each Cartesian direction. The first derivatives of the dipole moment with respect to atomic positions $\partial \vec{\mu} / \partial \xi_i$ are also computed. Each vibrational eigenmode leads to one peak in the absorption spectrum, at a frequency equal to the mode's eigenfrequency ν_{n0} . The absorption intensity corresponding to a particular eigenmode n whose eigenfrequency is ν_{n0} is given by

$$I_n = \frac{\pi}{3c} \left| \sum_{i=1}^{3N} \frac{\partial \vec{\mu}}{\partial \xi_i} \mathbf{l}_{\text{CART}in} \right|^2, \quad (3)$$

where $\mathbf{l}_{\text{CART}}$ is the matrix whose elements are the displacements of the atoms in Cartesian coordinates. The matrix $\mathbf{l}_{\text{CART}}$ is determined by the following procedure. First,

$$\mathbf{I}_{\text{CART}} = \mathbf{M} \mathbf{I}_{\text{MWC}} , \quad (4)$$

where $\mathbf{I}_{\text{MWC}}$ is the matrix whose elements are the displacements of the atoms in mass-weighted Cartesian coordinates and $\mathbf{M}$ is a diagonal matrix defined by the elements

$$M_{ii} = \frac{1}{\sqrt{m_i}} . \quad (5)$$

Proceeding, $\mathbf{I}_{\text{MWC}}$ is the matrix needed to diagonalize $\mathbf{f}_{\text{MWC}}$ defined by Eq.(2) such that

$$(\mathbf{I}_{\text{MWC}})^T \mathbf{f}_{\text{MWC}} (\mathbf{I}_{\text{MWC}}) = \Lambda , \quad (6)$$

where Λ is the diagonal matrix with eigenvalues λ_i . The procedure for diagonalizing Eq.(6) consists of the operations

$$\mathbf{f}_{\text{INT}} = (\mathbf{D})^T \mathbf{f}_{\text{MWC}} (\mathbf{D}) \quad (7)$$

and

$$(\mathbf{L})^T \mathbf{f}_{\text{MWC}} (\mathbf{L}) = \Lambda , \quad (8)$$

where $\mathbf{D}$ is a matrix transformation to coordinates where rotation and translation have been separated out and $\mathbf{L}$ is the transformation matrix composed of eigenvectors calculated according to Eq.(8). The eigenfrequencies in units of (cm^{-1}) are calculated using the eigenvalues λ_n by the expression

$$\nu_{n0} = \frac{\sqrt{\lambda_n}}{2\pi c} , \quad (9)$$

where c is the speed of light. The elements of $\mathbf{I}_{\text{CART}}$ are given by

$$I_{\text{CART}ki} = \sum_{j=1}^{3N} \frac{D_{kj} L_{ji}}{\sqrt{m_j}} , \quad (10)$$

where $k, i=1, \dots, 3N$, and the column vectors of these elements are the normal modes in Cartesian coordinates.

The intensity Eq.(3) must then be multiplied by the number density of molecules to give an absorption-line intensity in the non-interacting molecule approximation. It follows that the absorption spectrum calculated by GAUSSIAN is a sum of delta functions, whose line positions and coefficients correspond to the vibrational-transition frequencies and the absorption-line intensities, respectively. In principle, however, these spectral components must be broadened and shifted to account for anharmonic effects such as finite mode lifetimes and inter-mode couplings.

The DFT software GAUSSIAN09 (G09) can be used to compute an approximation of the UV absorption spectrum of a molecule or molecules by application of the formalism of time-dependent density functional theory (TD-DFT), which is described in reference [22].

Ground and Excited State Resonance Structure of Water Clusters Consisting of Randomly-Distributed Molecules

In this section are presented the results of computational investigations using DFT and TD-DFT concerning randomly-distributed water clusters of various size. These results include the relaxed or equilibrium configurations of water clusters ground-state oscillation frequencies and IR intensities, and oscillator strength as a function of excitation energy (within the UV range) for different geometries of

the interacting systems associated with stable structures, which are calculated by DFT and TD-DFT. For these calculations geometry optimization and vibrational analysis was effected using the DFT model B3LYP [30, 31] and basis function 6-311+G(d) [32, 33]. According to the specification of this basis function, (d) designates polarization functions having d functions for heavy atoms [34].

A graphical representation of molecular geometries of water clusters consisting of 2, 5, 12, 24 and 38 randomly-distributed molecules are shown in Figs. (1), (4), (7), (10) and (13), respectively. It is significant to note that the relative positions of the molecules associated with each of the molecular clusters is according to randomly selected positions of the water molecules prior to relaxation. The relaxed or equilibrium configurations of the water clusters consisting of 2, 5, 12, 24 and 38 randomly-distributed molecules are given in Tables 1, 4, 7, 10 and 13, respectively. The ground-state oscillation frequencies and IR intensities for the different molecular clusters, corresponding to their relaxed equilibrium configurations, are calculated by DFT according to the frozen phonon approximation. In the cases of water clusters consisting of 2, 5, 12, 24 and 38 randomly-distributed molecules, these values are given in Tables 2, 5, 8, 11 and 14, respectively. IR intensities as a function of frequency for the water clusters consisting of 2, 5, 12, 24 and 38 randomly-distributed molecules are shown in Figs. (2), (5), (8), (11) and (14), respectively.

Excitation energies and oscillator strengths of waters clusters of consisting of 2, 5, 12, 24 and 38 randomly-distributed molecules, after geometry optimization, which are calculated using TD-DFT, are given in Tables 3, 6, 9, 12 and 15. Correspondingly, the oscillator strength (UV intensity) as a function of excitation energy for the 2, 5, 12, 24 and 38 molecule water clusters are shown in Figs. (3), (6), (9), (12) and (15), respectively.

Ground and Excited State Resonance Structure of Liquid-Phase Water Clusters

In this section are presented the results of computational investigations using DFT and TD-DFT concerning liquid-phase water clusters of various size. These results include the relaxed or equilibrium configurations of water clusters ground-state oscillation frequencies and IR intensities, and oscillator strength as a function of excitation energy (within the UV range) for different geometries of the interacting systems associated with stable structures, which are calculated by DFT and TD-DFT. For these calculations geometry optimization and vibrational analysis was effected using the DFT model B3LYP [30, 31] and basis function 6-311+G(d) [32, 33]. According to the specification of this basis function, (d) designates polarization functions having d functions for heavy atoms [34]. The initial configuration of the liquid-phase clusters, prior to relaxation, was constructed using results of an 8 ps molecular dynamics simulations, which used model designations and parameters DFT/BLYP (code is CP2K, GTH pseudopotentials, DZVP basis, 280 eV cutoff), T=300 K, 0.5 fs time step, constant volume. The input to that simulation was a configuration from the end of a long (1 ns) flexible MM (potential was TIP3P) simulation with T=300 K and 0 pressure. The procedure of constructing the initial configuration of the liquid-phase clusters entailed cutting out clusters of whole water molecules which included all O atoms within some distance of a particular central O atom (distances are 2, 3, 4, 5, 6 Å).

A graphical representation of molecular geometries of liquid-phase water clusters consisting of 5, 12, 24 and 38 molecules are shown in Figs. (16), (19), (22) and (25), respectively. The relaxed or equilibrium configurations of the liquid-phase water clusters consisting of 5, 12, 24 and 38 molecules are given in Tables 16, 19, 22 and 25, respectively. The ground-state oscillation frequencies and IR intensities for the different molecular clusters, corresponding to their relaxed equilibrium configurations, are calculated by DFT according to the frozen phonon approximation. In the cases of liquid-phase water clusters consisting of 5, 12, 24 and 38 molecules, these values are given in Tables 17, 20, 23, and 26, respectively. IR intensities as a function of frequency for the liquid-phase water clusters consisting of 5, 12, 24 and 38 molecules are shown in Figs. (17), (20), (23) and (26), respectively.

Excitation energies and oscillator strengths of liquid-phase waters clusters of consisting of 5, 12, 24 and 38 molecules, after geometry optimization, which are calculated using TD-DFT, are given in Tables 18, 21, 24 and 27. Correspondingly, the oscillator strength (UV intensity) as a function of excitation energy for the 5, 12, 24 and 38 molecule water clusters are shown in Figs. (18), (21), (24) and (27), respectively.

Bond Paths For Equilibrium Configurations of Water Clusters

Presented in this section is an analysis of the electronic structure of water clusters in terms of the quantum topological property of electron density called the bond path. A bond path is the line along which the electron density is a maximum with respect to a neighboring line. Accordingly, if two atoms are bonded, their atomic volumes share a common interatomic surface, upon which there is a critical point where the gradient of the charge density is zero.

The theorem of Hohenberg & Kohn (HK) asserts that every quantum property of a molecular system is determined by the electron density, a mathematical object which is a function of the coordinates of only one particle at every local point in 3 dimensional space. This of course is vastly simpler than the wave function, an antisymmetric function of the coordinates of all N electrons in the molecular system, simultaneously occupying N different positions in space. The topological properties of the electron density allow an analysis which applies locally in the atomic space. Importantly, such a property is that of the bond path. This arises as follows. The full molecular electron density can be divided into its unique atomic components by the equation

$$\nabla \rho \cdot \bar{n} = 0 \quad (11)$$

where ρ is the charge density and $\bar{n}$ is a unit vector normal to the surface. The surfaces over which this equation holds serve to divide the molecule into its component atoms each of which is encapsulated within a zero flux surface. The atoms so defined are individual quantum systems which satisfy the virial theorem. The properties of these atoms deliver the corresponding properties of the full molecule by simple summation of the atomic properties. The bond path is a unique trajectory between pairs of bonding atoms defined as that path in real space along which at every point the electron density is a local maximum. The bond path may lie along a straight line between atomic nuclei, but is more generally a curved path between a bonded pair. Importantly, and there has been found to this no exception, bonding attractions between atoms are universally characterized by a bond path. If atoms are bonded by any chemical mechanism whatever, be it covalent, ionic, hydrogen bonding, London dispersion, etcetera, where a bonding attraction exists, so too does a corresponding bond path indicative thereof. It is not always obvious which atoms have bonding interactions in a molecule, so the existence of or lack of a bond path in the density is the ultimate criterion which may be used to decide the question. On every bond path between bonding atoms there exists a mathematical critical point called the bond critical point, which defines the extremities of the electron densities belonging to a bonding pair of atoms. The magnitude of the electron density at the bond critical point is a direct measure of the strength of the bonding interaction in force between the atoms. The bigger the density at the bond critical point the bigger is the bond strength between the atomic pair connected by a bond path. In summary, one may say the importance of the bond path is that it defines a molecular graph and serves as a universal indicator of the existence of bonding interactions, the strength of which is numerically measured by the electron density at the bond path critical point. Further discussion of quantum theory concerning bond paths is given in reference [35].

Shown in Tables 28 and 29 are denumerations of the different types of critical points associated with the electron density and calculated bond paths, i.e., bond critical point (BCP), ring critical point (RCP) and cage critical point (CCP), the AIMQB atomic properties. Shown in Table 30 are nets charges on the atoms for the different molecular clusters, i.e., the AIMQB net charge of the atoms. The

calculation of bond paths was done using the software AIMALL [36].

Conclusion

The DFT and TD-DFT calculated absorption spectra given here provide two types of information for general analysis of dielectric response. These are the denumeration of ground and excited state resonance modes and estimates of molecular level dielectric response structure. The calculations of ground and excited state resonance structure associated with disordered and ordered clusters of water molecules using DFT and TD-DFT are meant to serve as reasonable estimates of molecular level response characteristics, providing interpretation of dielectric response features, for subsequent adjustment relative to experimental measurements and additional constraints based on molecular structure theory. With respect to spectroscopic methods for detection or monitoring of target molecules within various types of water environments, i.e., different types of detection strategies and their associated algorithms for post-processing of measurements, the calculated resonance spectra presented here serve the purpose of isolating spectral features for correlating with the presence of water clusters.

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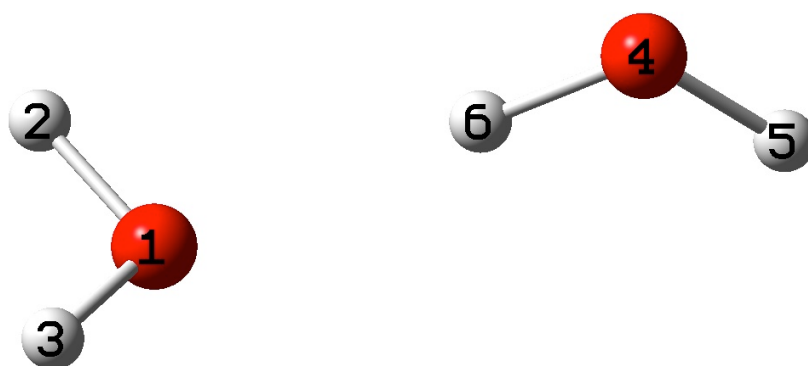


Figure 1. Molecular geometry of randomly-distributed water cluster consisting of 2 molecules, where relative location of atoms are given in Table 1.

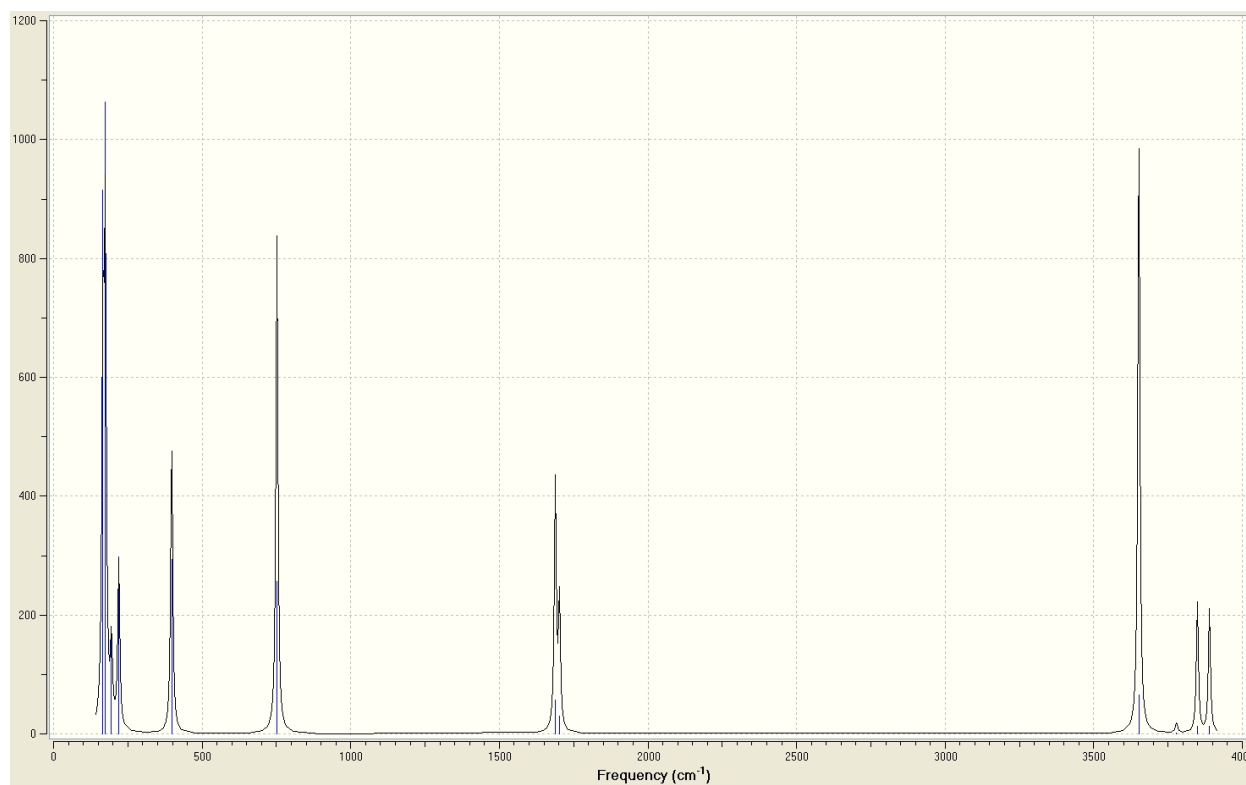


Figure 2. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for two-molecule randomly-distributed water cluster according to frozen phonon approximation.

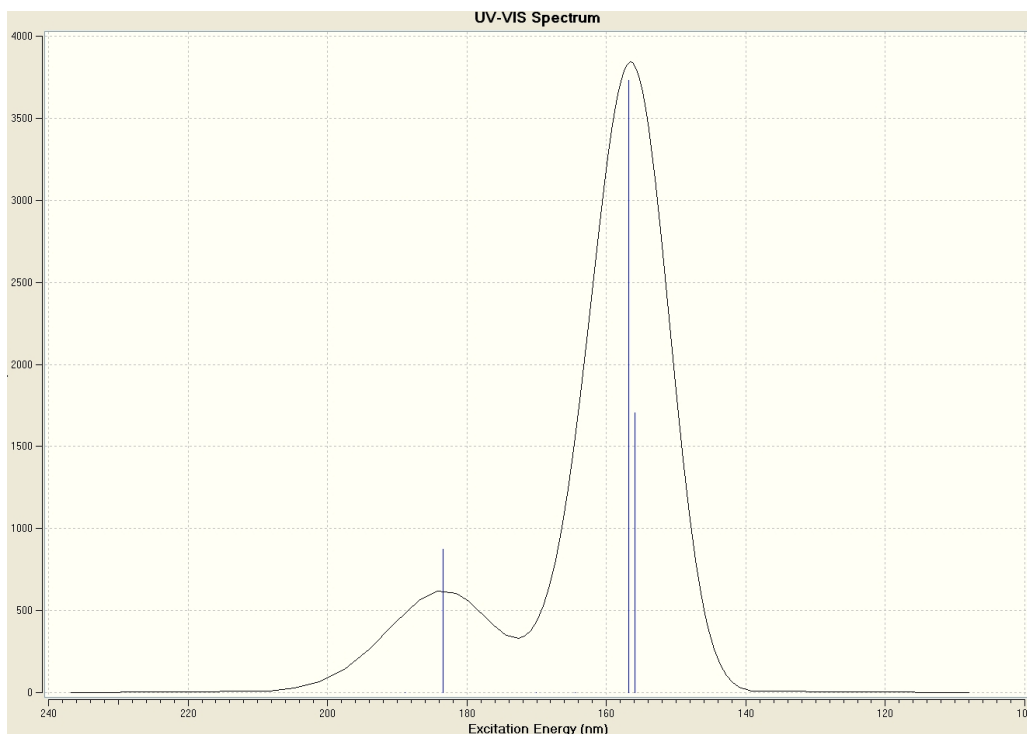


Figure 3. Oscillator strength as a function of excitation energy for two-molecule randomly-distributed water cluster calculated using TD-DFT.

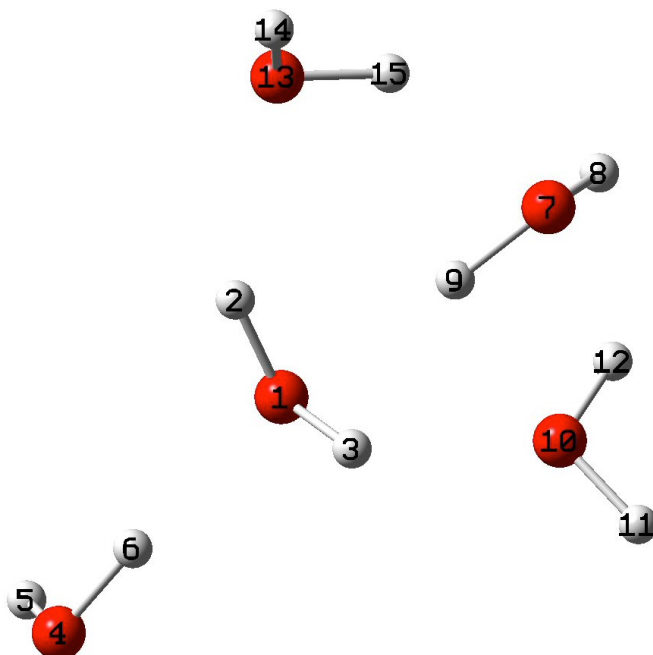


Figure 4. Molecular geometry of randomly-distributed water cluster consisting of 5 molecules, where relative location of atoms are given in Table 4.

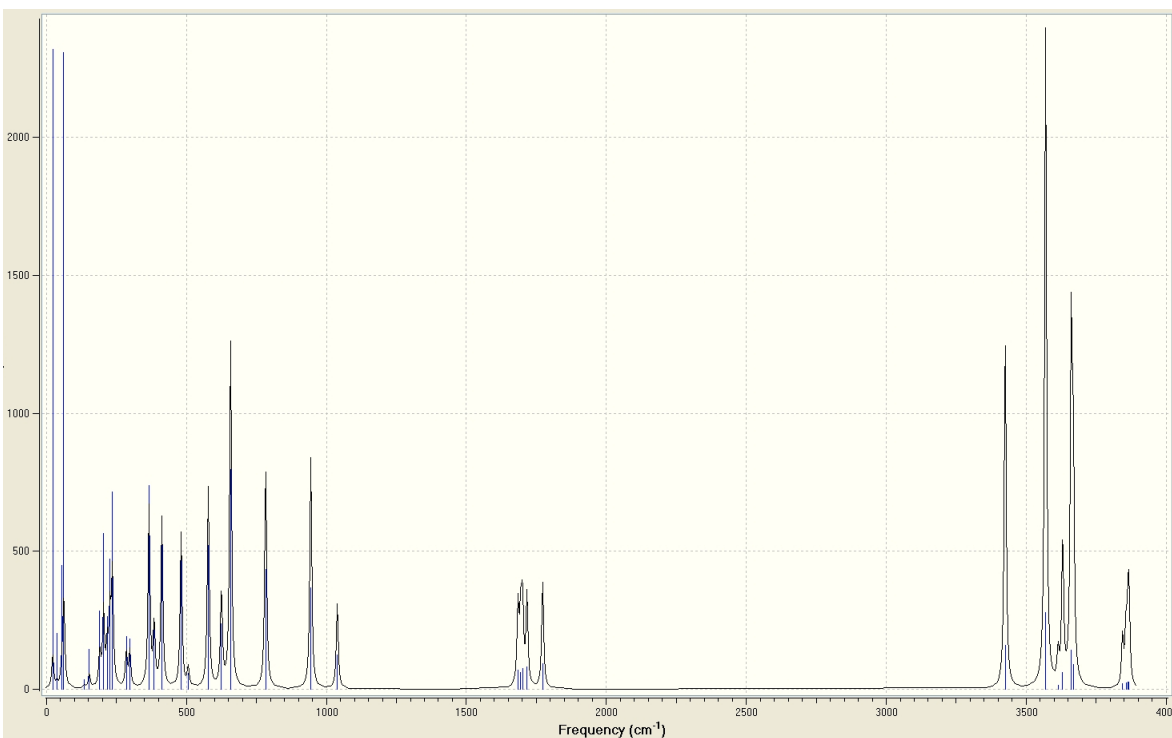


Figure 5. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for five-molecule randomly-distributed water cluster according to frozen phonon approximation.

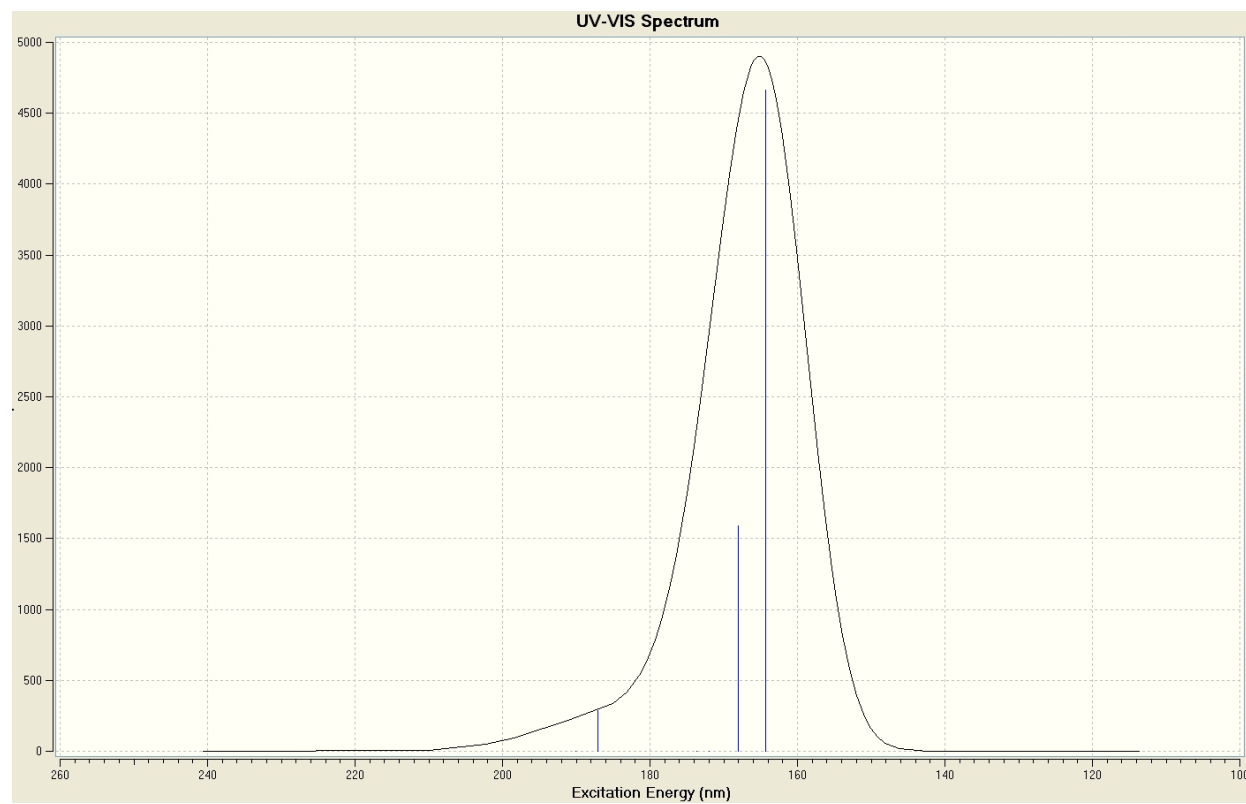


Figure 6. Oscillator strength as a function of excitation energy for five-molecule ($5\text{H}_2\text{O}$) randomly-distributed water cluster calculated using TD-DFT.

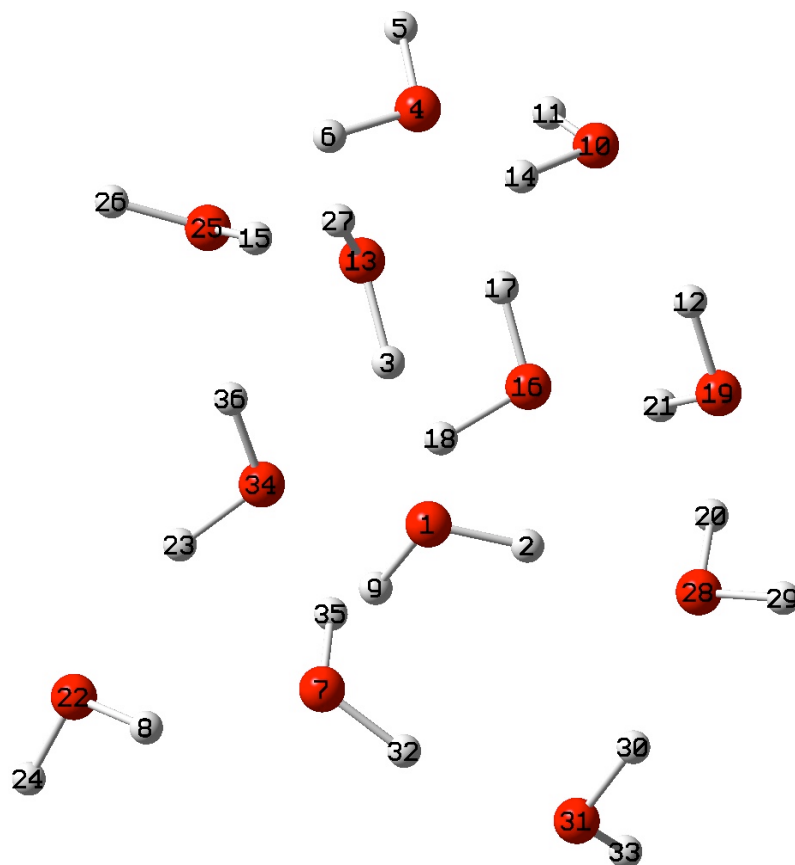


Figure 7. Molecular geometry of randomly-distributed water cluster consisting of 12 molecules, where relative location of atoms are given in Table 7.

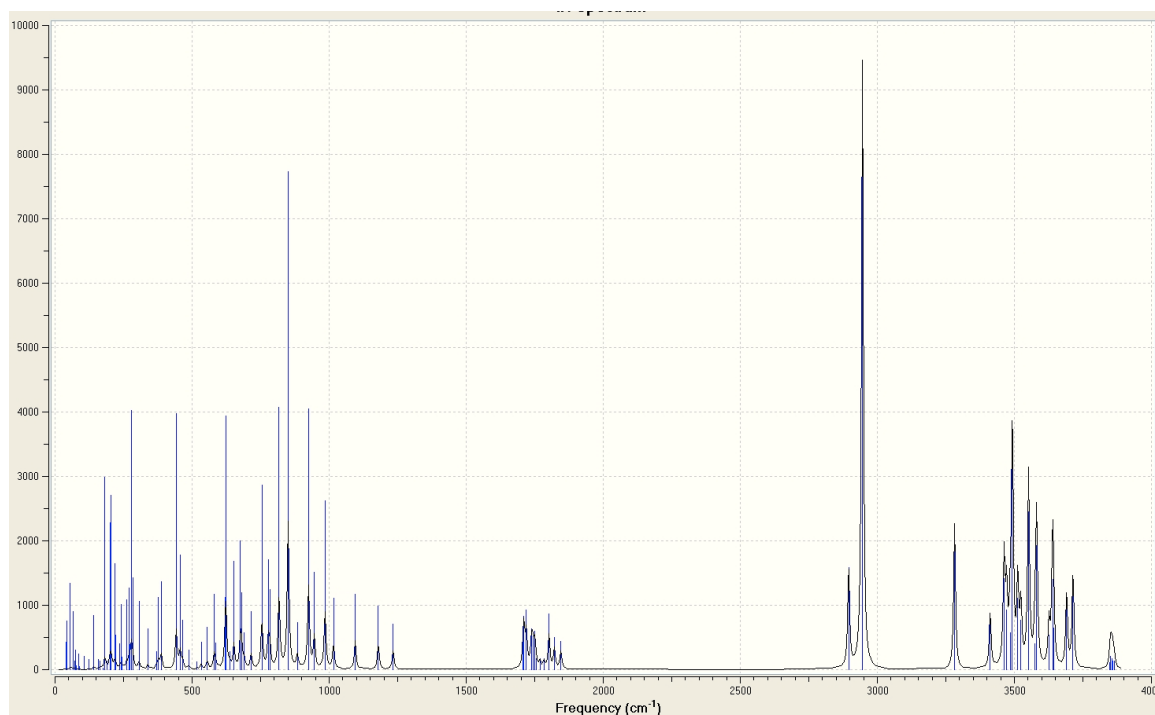


Figure 8. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for 12-molecule randomly-distributed water cluster according to frozen phonon approximation.

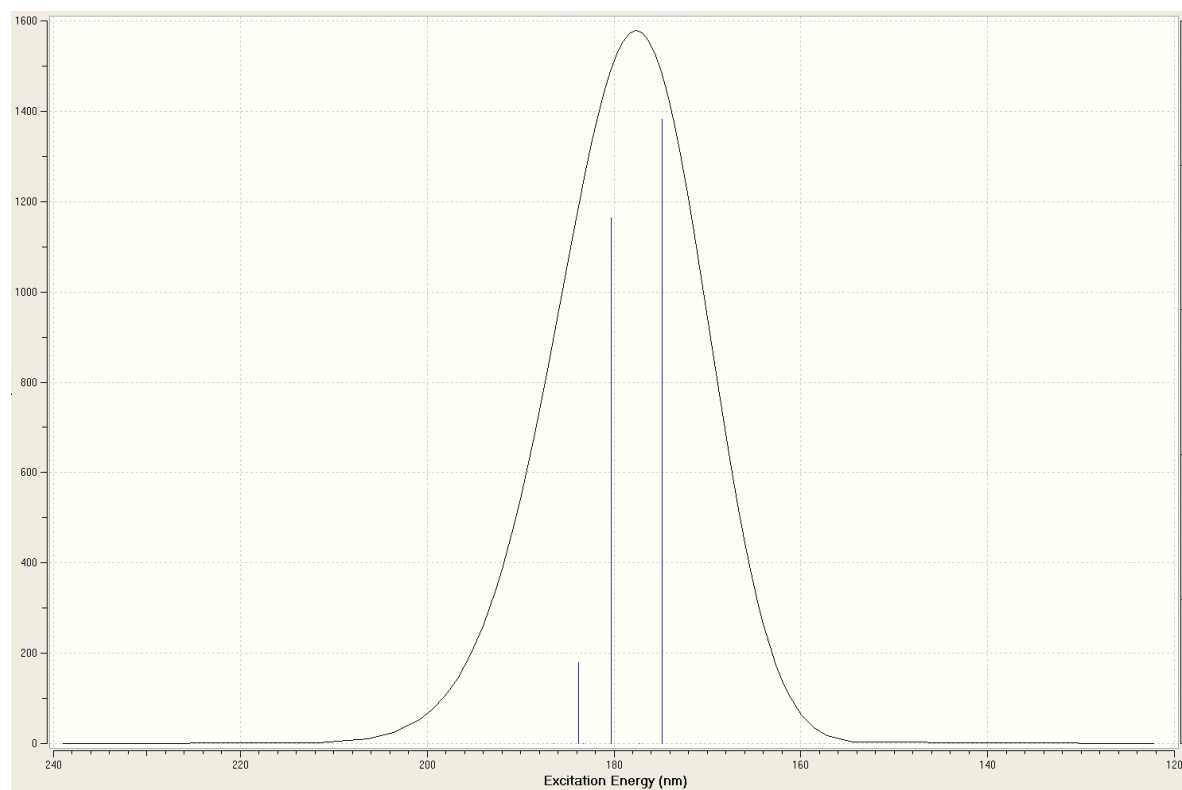


Figure 9. Oscillator strength as a function of excitation energy for 12-molecule ($12\text{H}_2\text{O}$) randomly-distributed water cluster calculated using TD-DFT.

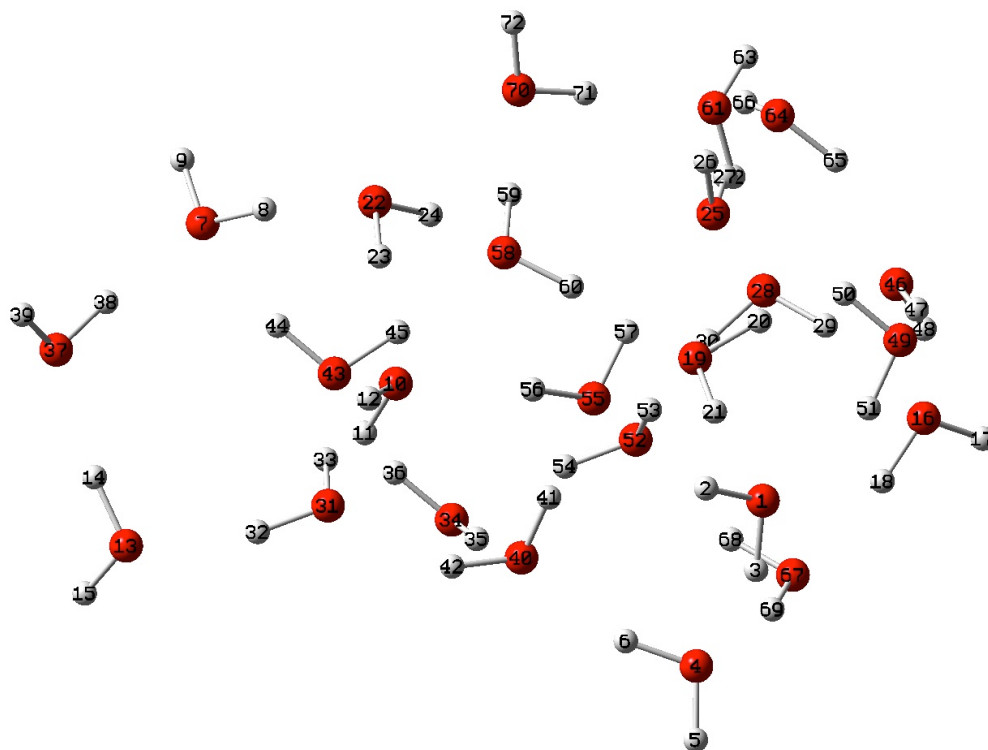


Figure 10. Molecular geometry of randomly-distributed water cluster consisting of 24 molecules, where relative location of atoms are given in Table 10.

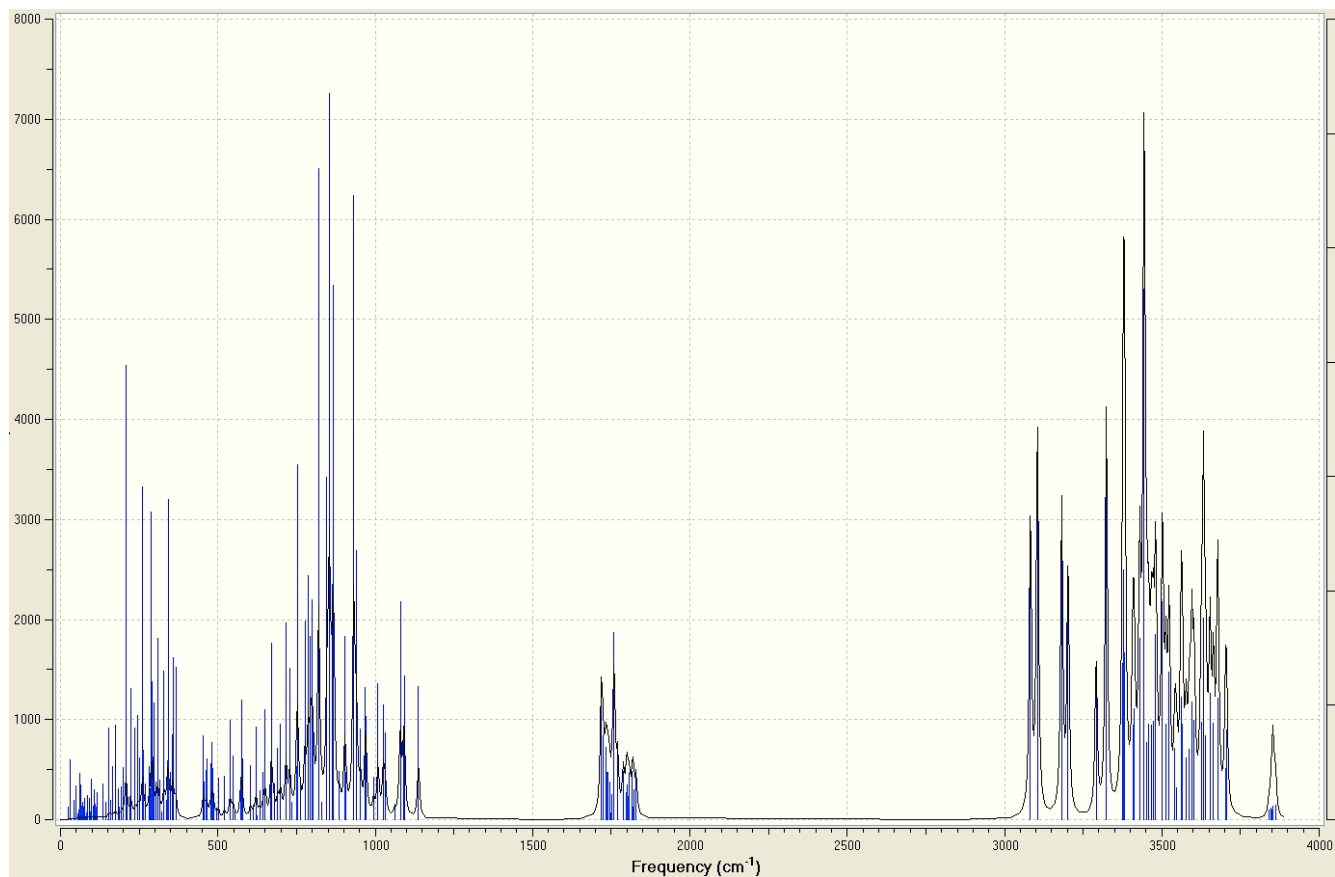


Figure 11. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for 24-molecule randomly-distributed water cluster according to frozen phonon approximation.

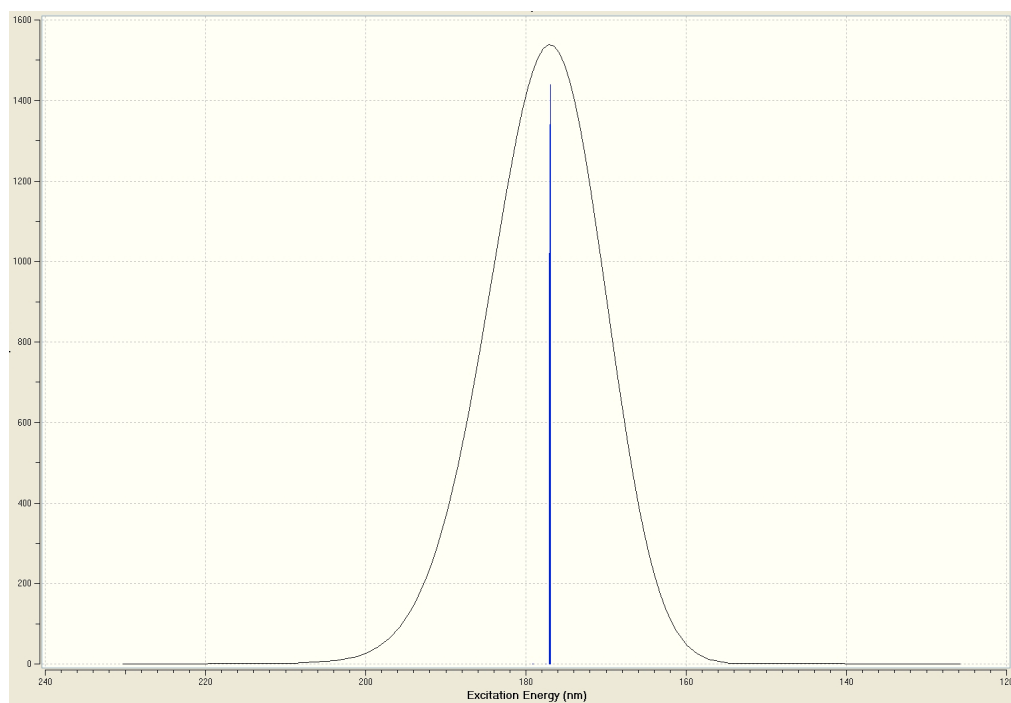


Figure 12. Oscillator strength as a function of excitation energy for 24-molecule ($24\text{H}_2\text{O}$) randomly-distributed water cluster calculated using TD-DFT.

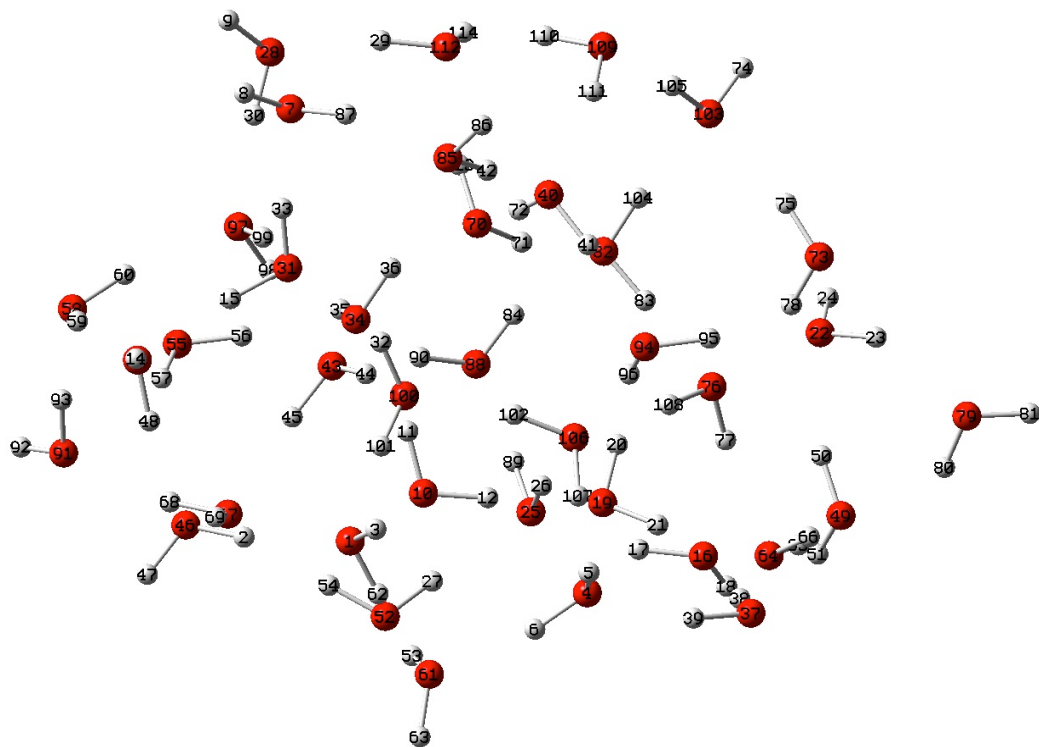


Figure 13. Molecular geometry of randomly-distributed water cluster consisting of 38 molecules, where relative location of atoms are given in Table 13.

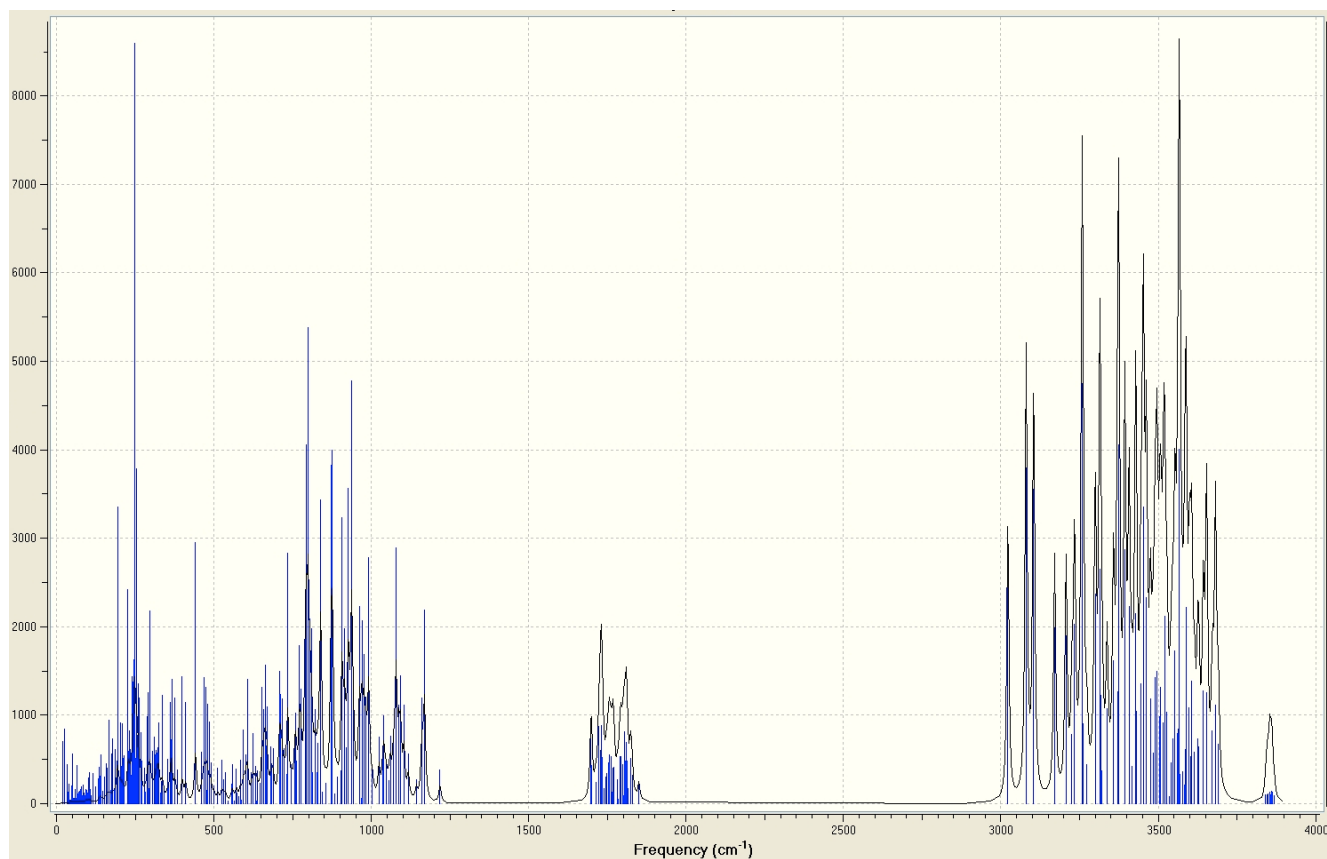


Figure 14. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for 38-molecule randomly-distributed water cluster according to frozen phonon approximation.

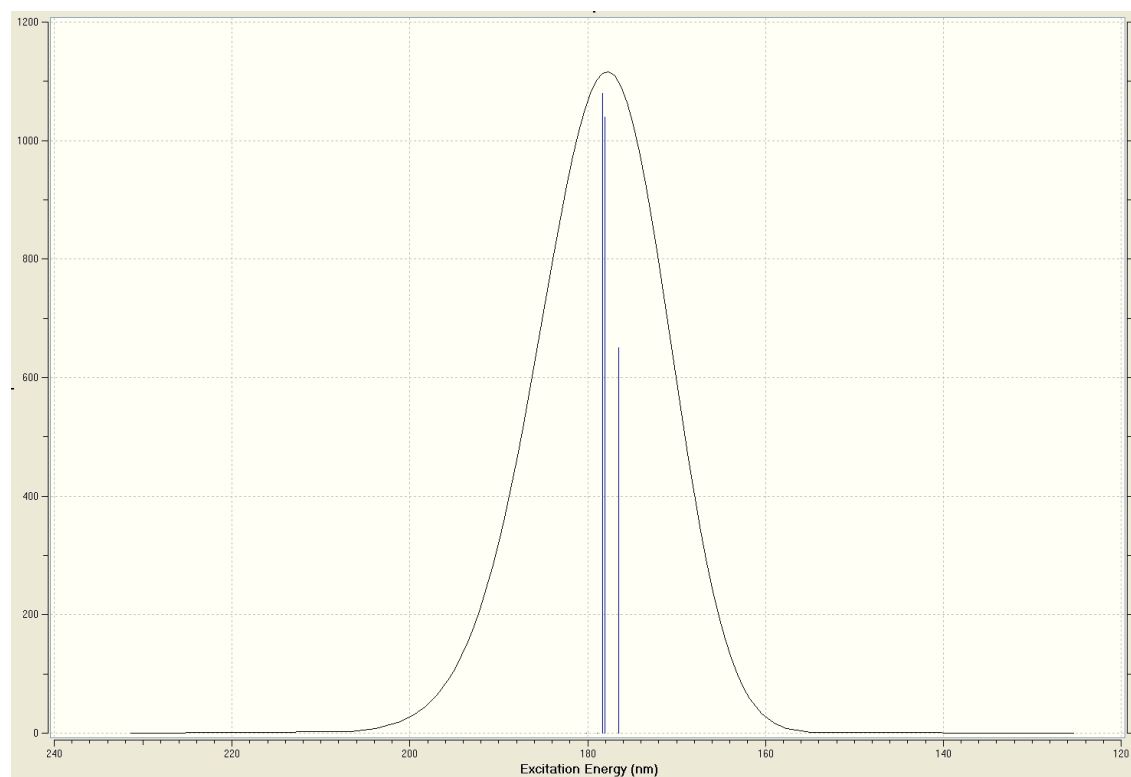


Figure 15. Oscillator strength as a function of excitation energy for 38-molecule ($38\text{H}_2\text{O}$) randomly-distributed water cluster calculated using TD-DFT.

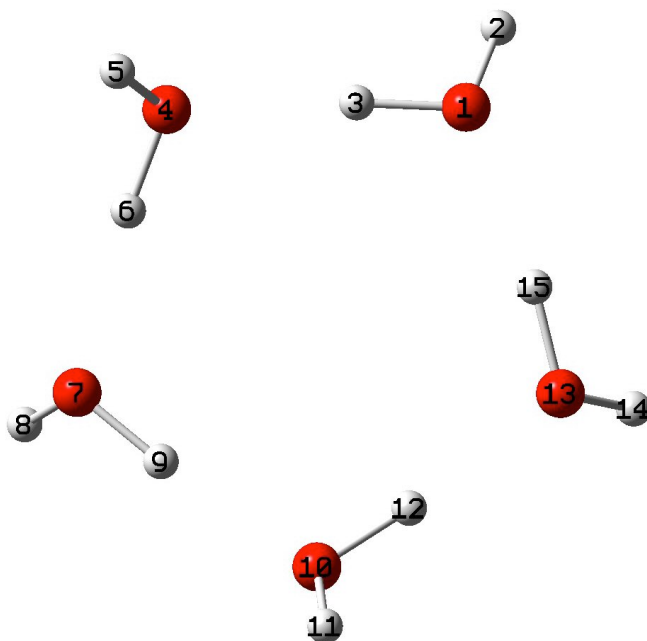


Figure 16. Molecular geometry of liquid-phase water cluster consisting of 5 molecules, where relative location of atoms are given in Table 16.

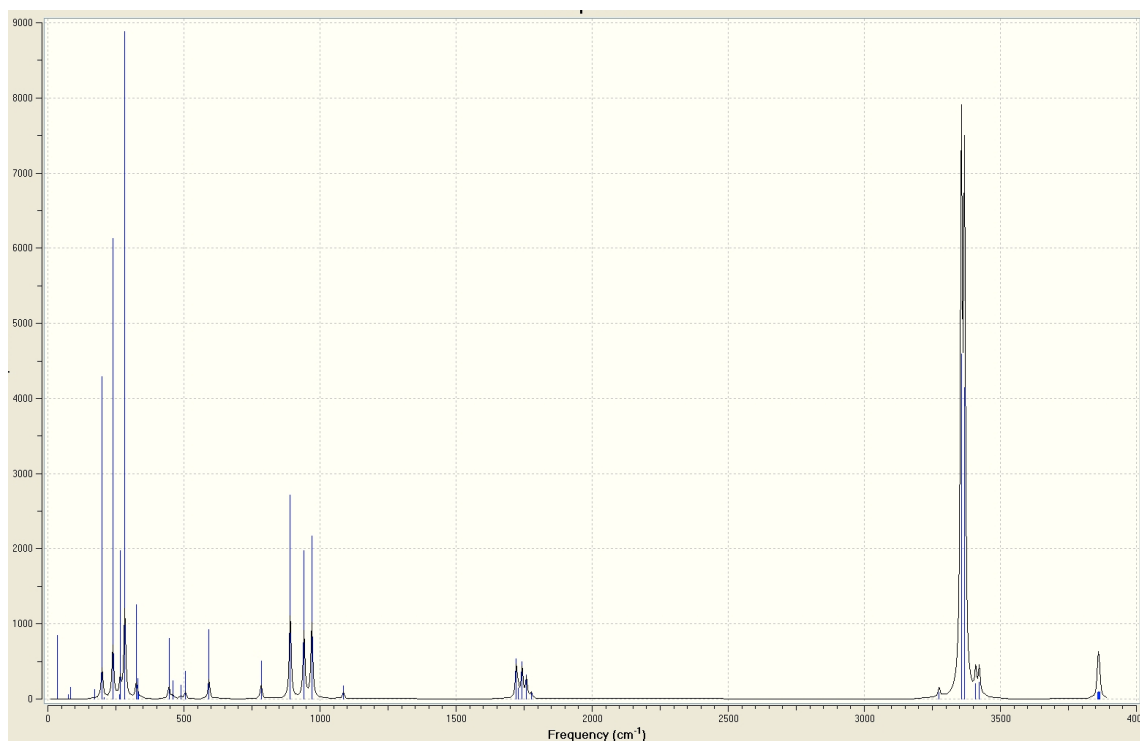


Figure 17. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for five-molecule liquid-phase water cluster according to frozen phonon approximation.

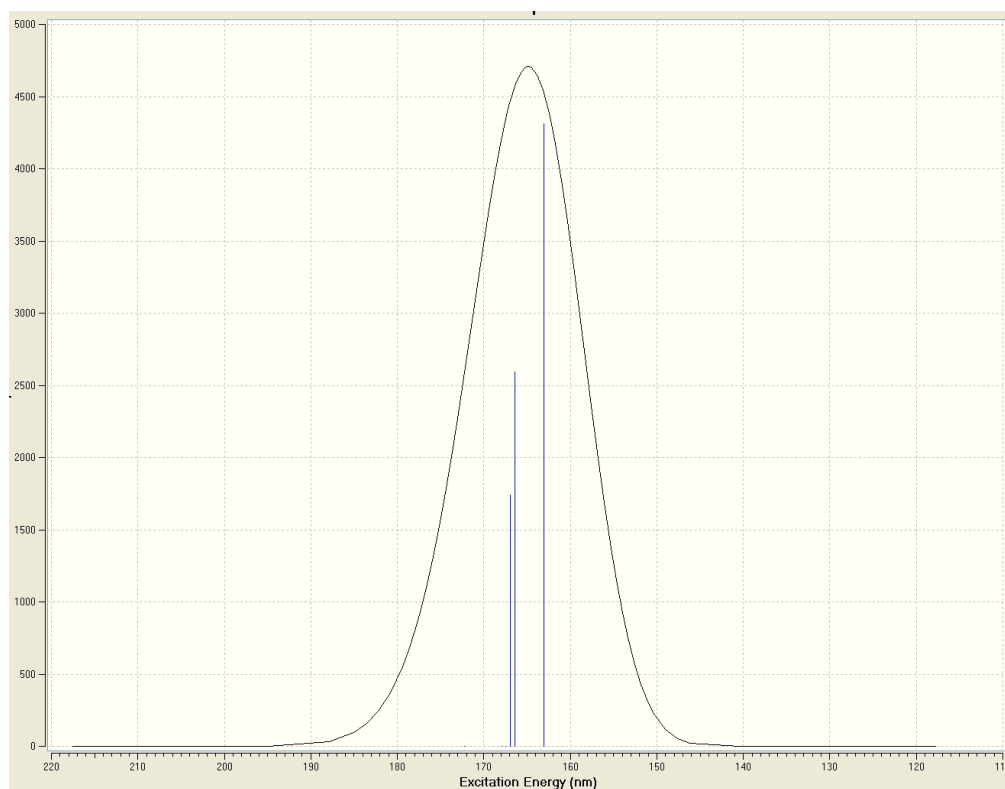


Figure 18. Oscillator strength as a function of excitation energy for five-molecule liquid-phase water cluster calculated using TD-DFT.

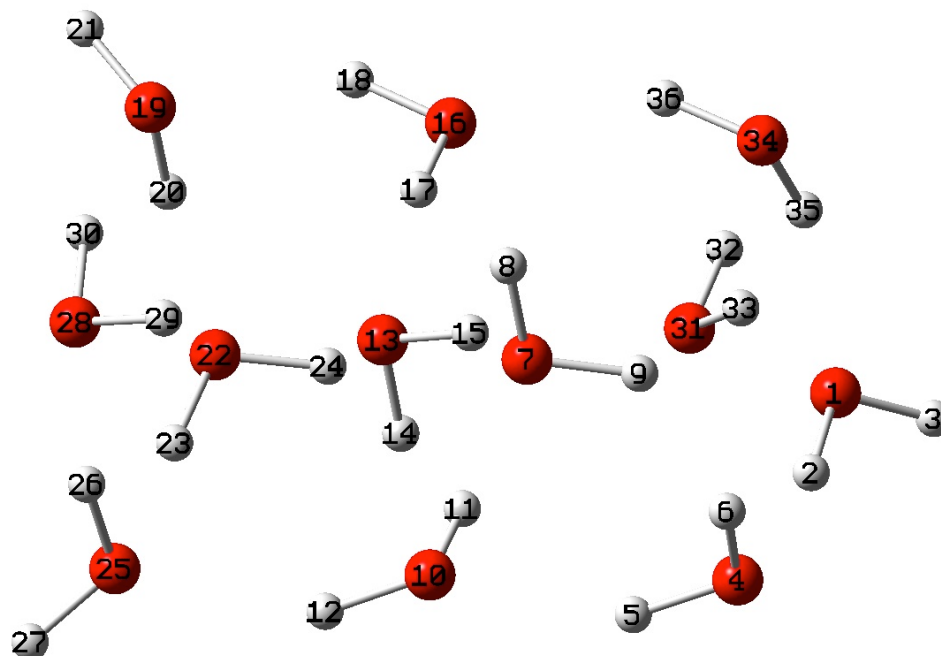


Figure 19. Molecular geometry of liquid-phase water cluster consisting of 12 molecules, where relative location of atoms are given in Table 19.

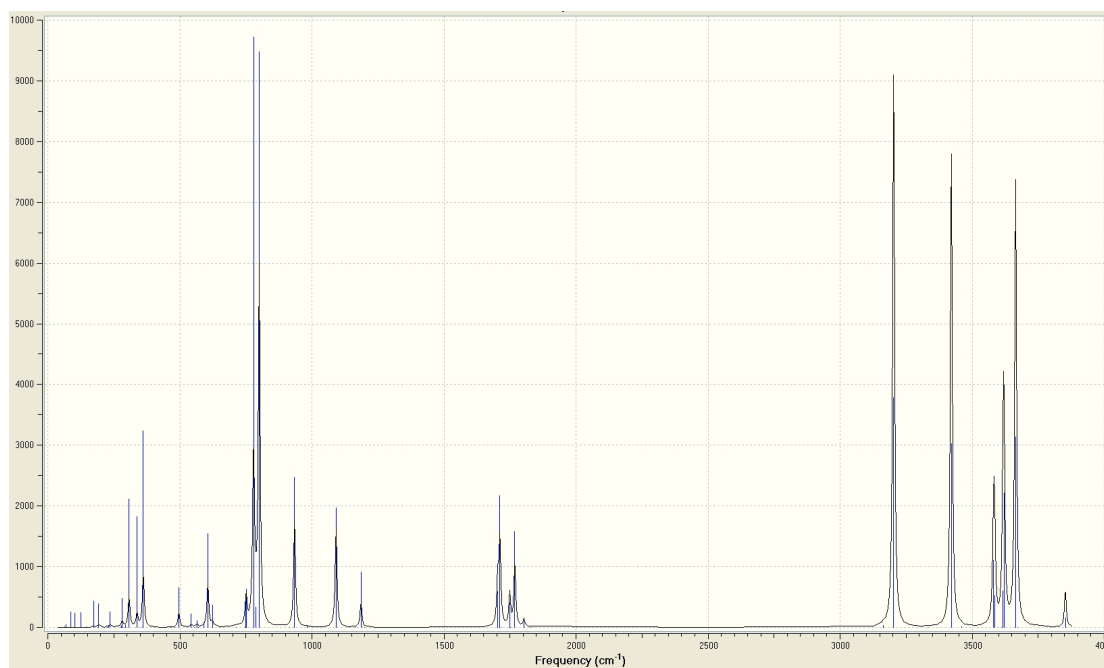


Figure 20. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for twelve-molecule liquid-phase water cluster according to frozen phonon approximation.

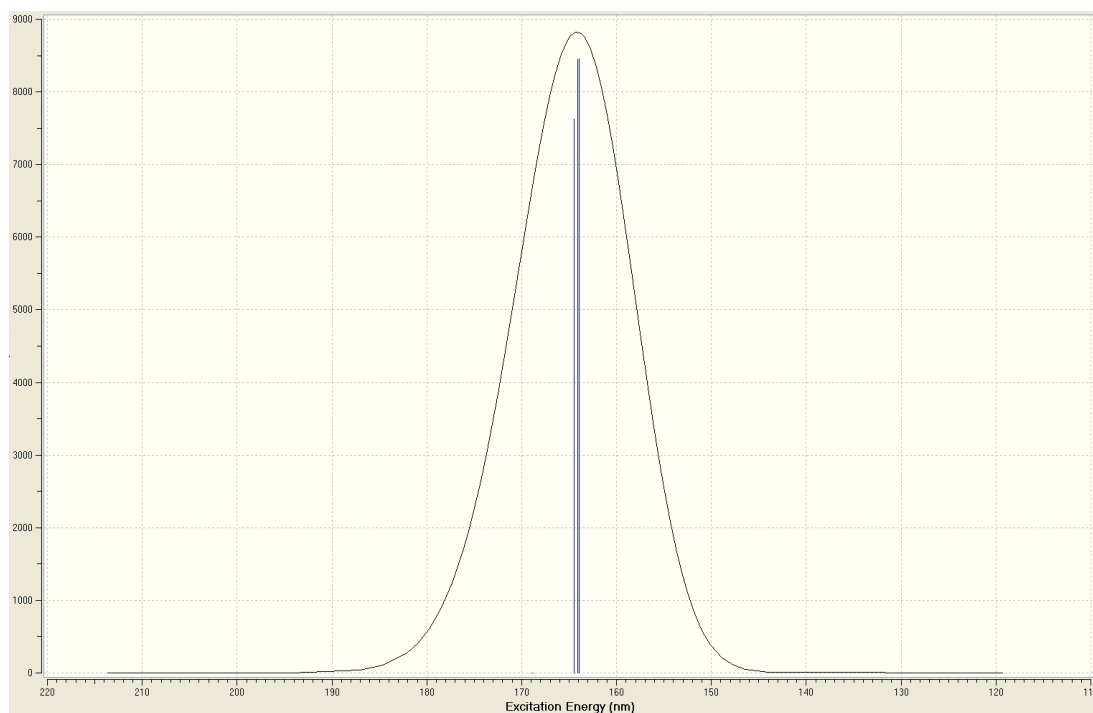


Figure 21. Oscillator strength as a function of excitation energy for 12-molecule ($12\text{H}_2\text{O}$) liquid-phase water cluster calculated using TD-DFT.

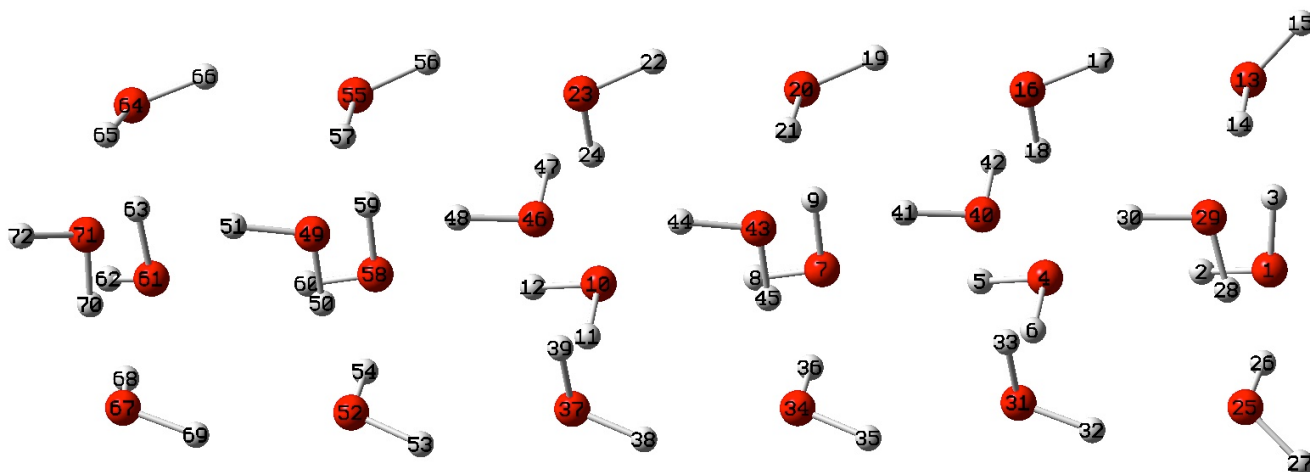


Figure 22. Molecular geometry of liquid-phase water cluster consisting of 24 molecules, where relative location of atoms are given in Table 22.

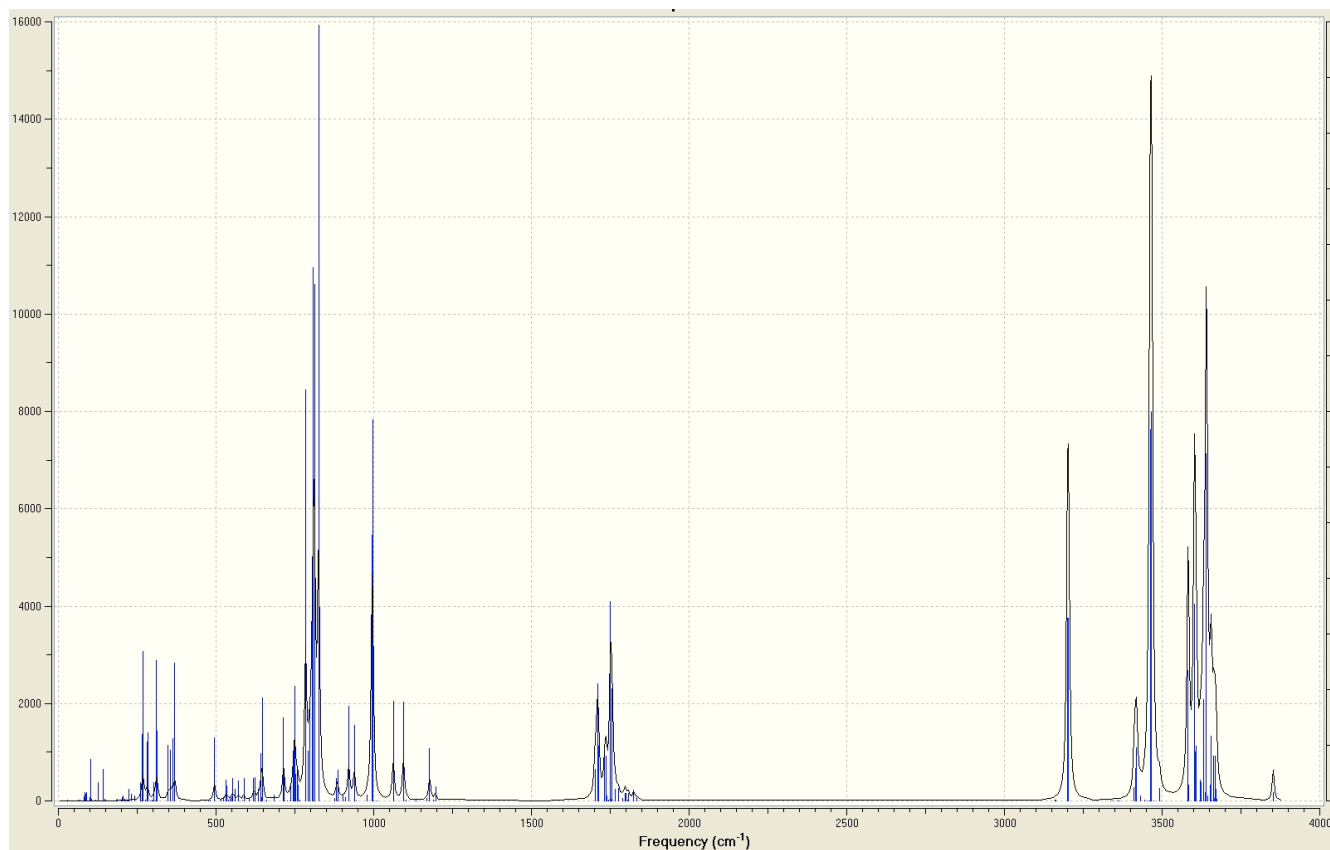


Figure 23. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for twentyfour-molecule ($24\text{H}_2\text{O}$) liquid-phase water cluster according to frozen phonon approximation.

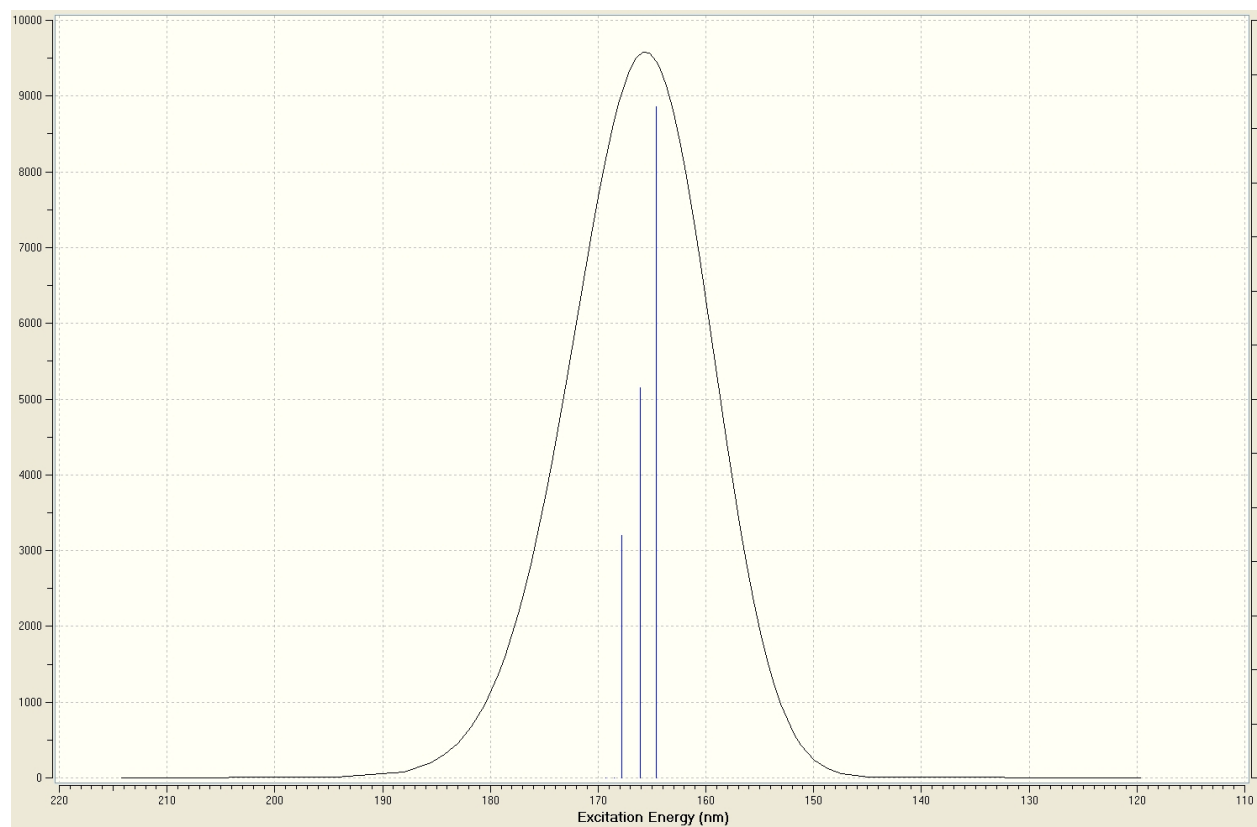


Figure 24. Oscillator strength as a function of excitation energy for 24-molecule liquid-phase water cluster calculated using TD-DFT.

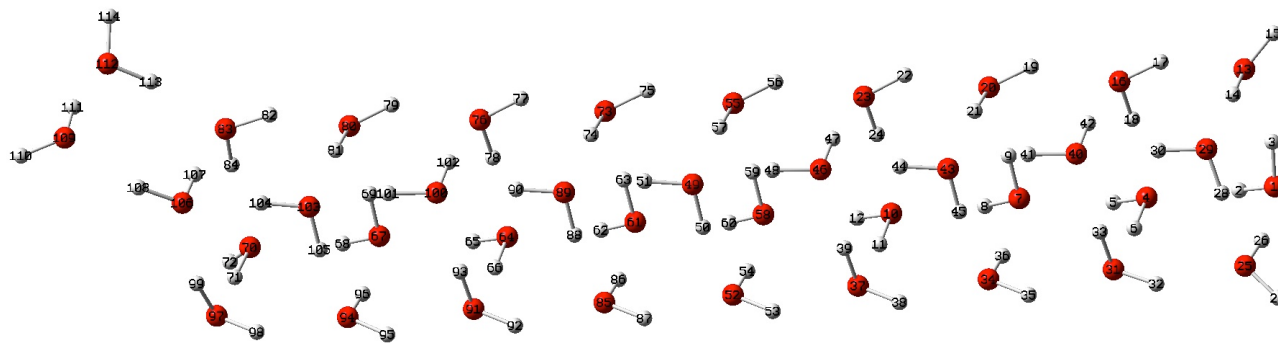


Figure 25. Molecular geometry of liquid-phase water cluster consisting of 38 molecules, where relative location of atoms are given in Table 25.

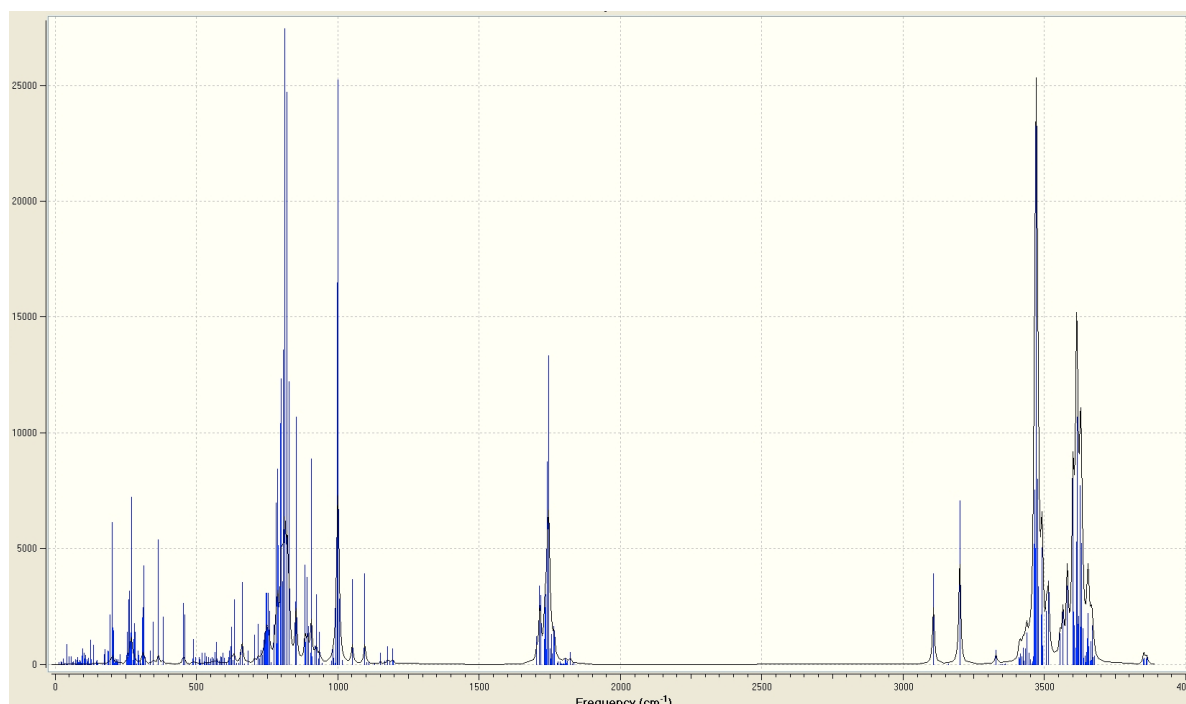


Figure 26. IR intensity as a function of frequency calculated using DFT B3LYP/6-311+G(d) for 38-molecule liquid-phase water cluster according to frozen phonon approximation.

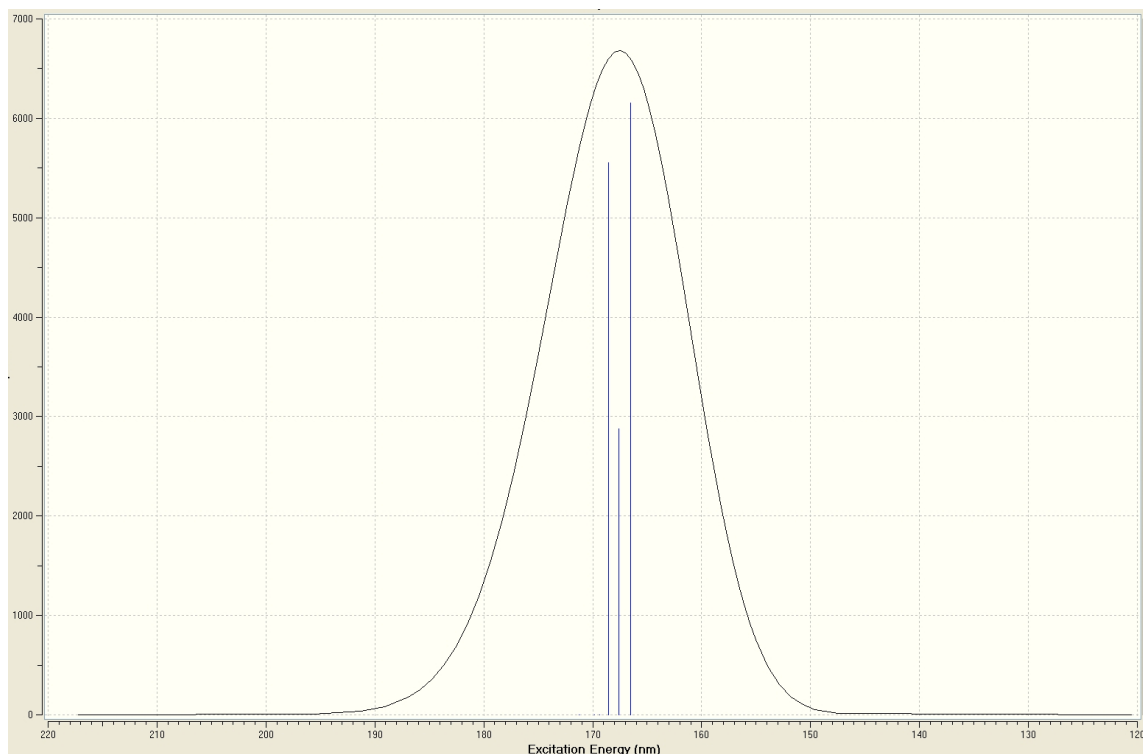


Figure 27. Oscillator strength as a function of excitation energy for 38-molecule liquid-phase water cluster calculated using TD-DFT.

Table 1. Atomic positions of two-molecule randomly-distributed water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	-0.0645	-0.0316	0.0673	4	O	2.2880	1.5115	0.5243
2	H	-0.7180	0.3448	-0.5324	5	H	3.0551	1.0188	0.2151
3	H	-0.5259	-0.2811	0.8756	6	H	1.5043	0.9703	0.3323

Table 2. Oscillation frequencies and IR intensities for two-molecule randomly-distributed water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
166.032	190.441	219.468	81.983	1688.305	121.363	3779.133	5.270
174.066	231.992	397.591	146.066	1702.229	63.010	3848.788	64.286
194.649	39.613	751.650	242.318	3651.812	297.915	3889.208	60.681

Table 3. Excitation energies and oscillator strengths for two-molecule randomly-distributed water cluster after geometry optimization calculated using TD-DFT, B3LYP/6-311+G(d).

Multiplicity-Orbital symmetry	Excitation Energy	Oscillator Strength
Triplet-A	188.85 nm	0.0000
Singlet-A	183.44 nm	0.0153
Triplet-A	170.05 nm	0.0000
Triplet-A	164.52 nm	0.0000
Singlet-A	156.79 nm	0.0653
Singlet-A	155.94 nm	0.0298

Table 4. Atomic positions of 5-molecule randomly-distributed water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	-0.3892	-0.5340	0.0950	9	H	1.1267	0.5034	-0.0211
2	H	-0.9629	0.1986	-0.1989	10	O	0.3298	0.4166	2.6025
3	H	-0.3778	-0.4882	1.0696	11	H	0.6748	0.0977	3.4420
4	O	-1.0865	-3.1551	-0.7176	12	H	1.0291	0.9141	2.1469
5	H	-0.7151	-3.3146	-1.5911	13	O	-1.0536	2.0878	-0.5191
6	H	-0.8542	-2.2415	-0.4705	14	H	-1.6463	2.7312	-0.1182
7	O	1.5651	1.3356	0.2667	15	H	-0.1472	2.2846	-0.2291
8	H	2.4104	1.4200	-0.1856					

Table 5. Oscillation frequencies and IR intensities for 5-molecule randomly-distributed water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
22.275	36.265	235.496	118.295	657.604	366.765	3569.180	694.013
37.418	5.290	285.070	38.235	782.954	238.824	3613.752	33.003
54.000	17.001	297.737	38.104	944.233	243.829	3630.182	156.364
61.750	99.946	366.253	189.530	1038.816	90.551	3660.857	367.215
133.982	3.123	384.600	65.515	1684.367	83.270	3668.187	231.370
152.785	15.650	412.189	177.995	1694.068	72.384	3844.127	52.612
190.272	37.828	480.956	163.642	1700.653	88.889	3856.304	60.170
203.706	80.700	506.087	20.677	1716.537	96.202	3863.952	69.727
217.110	39.993	577.873	211.040	1772.566	114.026	3867.5359	69.9327
226.665	74.887	624.908	104.212	3424.932	383.558		

Table 6. Excitation energies and oscillator strengths for 5-molecule (5H₂O) randomly-distributed water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital symmetry	Excitation Energy	Oscillator Strength
Triplet-A	190.05 nm	0.0000
Singlet-A	187.04 nm	0.0057
Triplet-A	173.62 nm	0.0000
Triplet-A	171.95 nm	0.0000
Singlet-A	168.03 nm	0.0318
Singlet-A	164.28 nm	0.0933

Table 7. Atomic positions of 12-molecule randomly-distributed water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	-0.8398	-0.7295	2.2261	19	O	0.8739	-2.5885	-0.9627
2	H	-0.9180	-1.6194	1.8292	20	H	-0.3402	-2.9139	0.0016
3	H	0.6445	-0.1462	2.2361	21	H	0.7313	-1.8690	-1.6149
4	O	3.2653	0.8075	-1.4471	22	O	-2.6973	3.1972	-0.4451
5	H	4.0371	1.1825	-1.8833	23	H	-1.1092	2.5397	-1.2059
6	H	2.8835	1.4841	-0.8514	24	H	-3.5005	3.6181	-0.7649
7	O	-2.4063	0.5866	0.3464	25	O	1.8225	2.2312	0.4378
8	H	-2.9343	2.3476	-0.0201	26	H	1.9500	3.0996	0.8333
9	H	-1.4708	-0.1659	1.7300	27	H	1.8826	0.2814	3.1373
10	O	3.0109	-1.4299	0.3553	28	O	-1.1116	-3.0432	0.6424
11	H	3.3048	-0.7706	-0.2953	29	H	-1.0956	-3.9544	0.9518
12	H	1.6823	-2.3282	-0.4701	30	H	-2.6046	-2.4113	-0.0738
13	O	1.5790	0.2358	2.2248	31	O	-3.3408	-1.8593	-0.4183
14	H	2.6023	-0.9283	1.0821	32	H	-2.8866	-0.2056	0.0188
15	H	1.7360	1.5690	1.1709	33	H	-3.5327	-2.1446	-1.3167
16	O	0.8211	-0.3200	-2.5629	34	O	-0.4535	1.8165	-1.2115
17	H	1.7192	0.0187	-2.4165	35	H	-1.6541	0.7442	-0.2589
18	H	0.2260	0.3986	-2.2862	36	H	0.2906	2.0755	-0.6382

Table 8. Oscillation frequencies and IR intensities for 12-molecule (12H₂O) disordered water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
39.196	1.686	269.44	34.303	715.519	64.918	2895.546	460.624
43.96	3.319	272.849	10.639	754.531	216.574	2945.704	2750.462
55.044	7.416	278.782	112.656	777.671	133.439	3281.943	659.819
65.298	0.94	284.507	40.627	783.778	98.069	3411.693	254.005
67.438	6.103	306.232	32.485	817.138	333.793	3462.534	489.183
71.292	1.001	339.513	21.552	850.378	659.013	3471.792	324.259
75.977	2.314	371.158	10.626	883.933	65.345	3484.279	198.352
77.832	0.432	377.707	42.578	924.913	375.647	3492.659	1128.253
85.896	2.144	387.239	53.078	945.8	143.561	3512.407	389.631
87.681	0.439	388.173	13.383	985.067	259.14	3523.923	271.01
106.792	2.172	442.26	176.274	1015.893	113.59	3551.773	874.987
122.294	1.924	456.408	81.336	1095.177	128.823	3575.075	143.702
141.487	11.935	465.251	35.668	1179.576	116.762	3581.117	689.982
158.59	2.47	488.3	14.754	1233.467	87.228	3626.239	193.201
164.348	2.158	518.638	6.401	1708.321	81.28	3639.376	511.275
175.615	0.333	533.348	22.544	1710.876	141.219	3642.695	238.247
181.907	54.415	555.373	36.399	1719.412	159.932	3690.683	346.948
190.745	2.495	580.737	68.305	1738.189	110.549	3713.902	447.436
200.214	45.809	586.705	24.474	1742.994	92.161	3848.289	42.322
204.584	55.602	621.544	70.183	1749.713	104.636	3851.638	80.48
217.211	35.795	623.176	246.263	1754.469	29.166	3851.824	26.924
222.688	12.065	637.781	17.871	1769.095	31.031	3856.421	67.288
235.415	9.502	652.63	109.943	1783.692	30.106	3859.586	51.399
242.275	24.697	676.299	135.332	1802.249	156.947	3864.981	54.253
243.905	4.627	680.527	81.169	1821.899	91.974		
261.031	28.411	689.975	40.03	1845.457	81.575		

Table 9. Excitation energies and oscillator strengths for 12-molecule (12H₂O) randomly-distributed water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital Symmetry	Excitation Energy	Oscillator Strength
Triplet-A	186.43 nm	0.0000
Singlet-A	183.78 nm	0.0028
Triplet-A	183.25 nm	0.0000
Singlet-A	180.31 nm	0.0182
Triplet-A	177.24 nm	0.0000
Singlet-A	174.83 nm	0.0216

Table 10. Atomic positions of 24-molecule randomly-distributed water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	1.6734	-2.4094	1.8612	37	O	-6.8000	0.8410	-0.5654
2	H	0.7839	-2.2578	2.2277	38	H	-6.0084	1.4224	-0.5863
3	H	1.6481	-3.2010	1.2935	39	H	-7.4259	1.2161	0.0611
4	O	1.2173	-4.0863	-0.2909	40	O	-1.0064	-2.4938	-0.1535
5	H	1.1134	-5.0302	-0.4492	41	H	-0.7686	-1.8704	0.5614
6	H	0.3334	-3.6628	-0.3758	42	H	-1.9839	-2.5372	-0.1303
7	O	-4.5104	2.3620	-0.6088	43	O	-2.6542	0.4322	-1.5807
8	H	-3.9421	2.3149	0.2144	44	H	-3.3391	1.1234	-1.5715
9	H	-4.5532	3.2811	-0.8920	45	H	-1.8744	0.8160	-1.1148
10	O	-3.3241	-0.5769	2.4161	46	O	4.2458	0.4616	1.0866
11	H	-3.5283	-1.0195	1.5481	47	H	4.1621	-0.0585	1.9189
12	H	-3.9634	-0.8772	3.0698	48	H	4.7814	-0.0252	0.4330
13	O	-6.2268	-1.8110	-0.6298	49	O	3.3418	-0.7349	3.3364
14	H	-6.5176	-0.8709	-0.6266	50	H	2.6260	-0.0887	3.4686
15	H	-6.6076	-2.2384	-1.4027	51	H	2.9061	-1.5260	2.9724
16	O	5.1753	-0.8848	-1.1480	52	O	1.6993	-0.5744	-2.5469
17	H	6.0507	-1.1590	-1.4391	53	H	1.5964	-0.3880	-1.5887
18	H	4.5470	-1.6335	-1.3367	54	H	0.7979	-0.7812	-2.8804
19	O	1.6703	-0.1132	0.1759	55	O	-0.5783	-0.9557	2.2524
20	H	2.5483	0.2641	0.4033	56	H	-1.5015	-0.8266	2.5397
21	H	1.6355	-0.9430	0.6939	57	H	-0.0678	-0.1496	2.4699
22	O	-2.8700	2.0418	1.4422	58	O	-0.6198	1.5486	-0.1134
23	H	-3.0952	1.2238	1.9221	59	H	-0.2828	2.3889	-0.5002
24	H	-1.9853	1.8956	1.0446	60	H	0.1560	0.9868	0.0910
25	O	1.1454	1.1954	3.0591	61	O	2.9964	3.4655	-1.2645
26	H	0.8744	1.7368	3.8083	62	H	3.2844	2.6308	-1.7356
27	H	1.6220	1.7989	2.4335	63	H	3.6214	4.1553	-1.5098
28	O	3.7513	1.2500	-2.5093	64	O	2.8028	2.7310	1.5350
29	H	4.3618	0.6328	-2.0669	65	H	3.5401	2.0965	1.4405
30	H	2.9939	0.7027	-2.8009	66	H	2.7117	3.1216	0.6495
31	O	-3.5978	-1.6208	-0.0328	67	O	3.3186	-2.6699	-1.8644
32	H	-4.5258	-1.8415	-0.2784	68	H	2.7153	-2.0391	-2.3160
33	H	-3.3092	-0.8864	-0.6273	69	H	2.7529	-3.2157	-1.2947
34	O	-0.8829	-1.3723	-2.8395	70	O	0.3034	3.8930	-1.1482
35	H	-0.9006	-1.8260	-1.9782	71	H	1.2686	3.8141	-1.3148
36	H	-1.5823	-0.7005	-2.7835	72	H	0.1676	4.6829	-0.6155

Table 11. Oscillation frequencies and IR intensities for 24-molecule (24H₂O) randomly-distributed water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
24.61	0.35	270.30	10.52	735.58	13.66	1819.22	24.63
31.60	2.06	280.27	14.22	749.76	43.28	1821.92	59.14
34.75	0.04	282.90	16.50	752.62	293.12	1829.53	100.30
42.55	0.91	284.92	9.71	761.44	35.03	3082.34	913.99
48.14	1.78	288.84	97.46	776.74	168.97	3104.57	1187.46
54.16	0.35	290.90	43.96	787.11	210.57	3181.76	914.96
58.55	0.60	293.18	20.10	794.50	159.22	3201.93	762.65
61.81	1.55	295.82	37.79	799.36	192.50	3291.18	475.00
62.13	3.14	302.90	12.54	803.30	86.34	3323.75	1195.07
65.46	2.47	309.02	61.51	820.24	585.34	3376.50	576.95
68.88	1.03	309.60	18.02	829.20	16.04	3379.65	926.26
70.87	0.53	315.53	13.67	846.82	318.07	3381.92	618.94
71.96	1.40	320.92	2.74	854.25	680.23	3407.76	352.59
73.41	1.03	326.93	18.49	862.40	222.53	3411.85	413.88
76.96	1.79	329.01	53.43	867.98	508.61	3429.60	682.42
80.37	0.16	337.05	7.28	886.25	46.47	3443.66	2000.48
82.98	0.62	339.66	21.75	903.26	181.13	3451.97	293.21
84.37	2.26	341.66	119.98	906.29	46.99	3458.29	360.61
90.54	1.21	349.89	17.96	931.83	636.93	3466.60	357.61
91.09	2.07	355.73	32.92	940.10	276.83	3472.47	373.19
95.52	0.76	357.09	63.28	953.23	94.51	3480.60	704.68
99.44	4.41	366.51	61.15	969.31	140.41	3502.00	835.75
103.42	1.48	452.97	41.50	970.04	109.39	3513.10	366.07
106.04	3.45	455.45	18.56	995.11	46.71	3523.19	568.31
109.55	1.83	461.17	24.83	1009.00	150.27	3542.09	275.24
114.14	1.62	465.68	30.80	1025.57	129.08	3547.81	121.96
116.86	0.69	477.13	29.09	1031.70	98.46	3561.43	478.37
117.42	3.48	481.64	40.92	1061.58	18.28	3565.18	371.20
133.68	1.09	484.58	27.24	1079.77	257.49	3577.25	242.53
135.85	5.29	488.04	14.05	1090.24	95.69	3587.46	277.33
142.90	2.66	497.27	6.27	1092.32	172.35	3595.25	462.06
148.77	0.08	502.10	22.77	1137.81	166.02	3602.69	393.14
152.07	3.14	521.75	24.90	1718.33	212.50	3625.53	387.03
154.45	15.47	538.56	58.73	1719.19	132.08	3631.20	108.16
160.67	3.38	548.02	38.10	1724.16	158.74	3632.65	800.94
164.76	9.49	552.85	5.32	1732.43	137.19	3639.88	333.52
174.57	18.12	571.57	26.29	1736.40	89.03	3653.21	506.91
183.12	6.14	574.69	75.09	1740.66	91.06	3663.94	386.88
184.95	1.30	577.65	38.68	1744.53	72.82	3676.89	489.39
186.06	2.51	604.01	35.82	1747.36	13.55	3678.61	309.44
192.01	6.81	613.50	9.86	1752.47	9.38	3702.04	208.80

Table 11 (continued). Oscillation frequencies and IR intensities for 24-molecule (24H₂O) randomly-distributed water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
197.68	11.32	621.17	62.86	1753.38	47.34	3705.28	365.79
207.75	103.37	623.46	2.46	1757.12	64.03	3840.72	40.62
209.18	12.11	633.49	20.10	1759.44	360.44	3848.14	47.00
211.24	7.38	643.65	33.01	1770.28	151.94	3849.72	40.22
220.53	5.66	650.33	78.62	1788.08	93.88	3852.54	58.65
223.04	11.25	668.03	42.31	1790.17	33.80	3853.57	54.69
224.97	32.29	671.36	129.77	1796.95	3.98	3853.74	57.97
237.29	23.80	678.97	26.88	1798.18	52.92	3854.45	43.22
245.99	27.95	690.60	54.35	1800.17	68.68	3861.18	53.38
251.17	16.90	699.79	73.37	1802.72	44.86	3861.73	62.52
260.31	94.79	716.55	154.38	1807.95	91.09		
262.67	19.87	728.16	121.12	1817.39	95.23		

Table 12. Excitation energies and oscillator strengths for 24-molecule (24H₂O) randomly-distributed water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital symmetry	Excitation Energy	Oscillator Strength
Triplet-A	179.20 nm	0.0000
Triplet-A	179.08 nm	0.0000
Triplet-A	177.49 nm	0.0000
Singlet-A	177.08 nm	0.0102
Singlet-A	177.00 nm	0.0134
Singlet-A	176.93 nm	0.0144

Table 13. Atomic positions of 38-molecule randomly-distributed water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	-1.3740	-3.0674	1.2453	58	O	-6.2909	-0.1480	-0.7221
2	H	-2.9882	-3.2666	0.9267	59	H	-6.1230	-0.4051	0.1997
3	H	-0.9680	-2.9052	2.1434	60	H	-5.6226	0.5307	-0.9411
4	O	2.2351	-3.1144	0.2781	61	O	0.0667	-4.6996	-0.4342
5	H	2.2666	-2.8925	1.2372	62	H	-0.8447	-3.7377	0.7661
6	H	1.5456	-3.7862	0.1067	63	H	0.1000	-5.6612	-0.4547
7	O	-3.3675	3.1125	2.8591	64	O	5.0259	-2.3282	3.1320
8	H	-4.0573	3.1629	3.5286	65	H	5.3749	-2.0101	2.2670
9	H	-4.7677	4.5967	-0.6057	66	H	5.6146	-2.0026	3.8197
10	O	-0.2688	-2.3644	3.5426	67	O	-3.4988	-2.6693	-2.2243
11	H	-0.6608	-1.4944	3.7434	68	H	-4.4179	-2.6110	-2.5677
12	H	0.6967	-2.2469	3.4312	69	H	-3.6104	-2.8341	-1.2681
13	O	-5.0172	-0.9714	1.7452	70	O	-0.5079	2.2349	-0.7999
14	H	-4.9798	-1.0434	2.7208	71	H	0.1598	2.1421	-1.5121
15	H	-3.8222	0.2252	1.4993	72	H	0.1784	2.4097	0.7667
16	O	3.5985	-1.8742	-3.7327	73	O	4.6529	2.6979	-1.1774
17	H	2.6125	-1.9440	-3.7853	74	H	2.9191	5.4176	-2.1456
18	H	3.9734	-2.1863	-4.5623	75	H	4.0040	3.4161	-1.2853
19	O	2.3751	-1.9513	2.7678	76	O	3.3386	0.5692	-2.4118
20	H	2.4108	-1.0103	2.4932	77	H	3.6493	-0.1355	-3.0107
21	H	3.2793	-2.1646	3.0944	78	H	4.3337	1.9522	-1.7199
22	O	5.0283	1.3456	1.0936	79	O	7.5037	0.4080	1.9929
23	H	5.9003	1.3893	1.5249	80	H	7.2783	-0.3740	1.4531
24	H	4.9954	1.9663	0.3242	81	H	8.4253	0.6325	1.8330
25	O	0.9312	-1.7123	-3.3628	82	O	1.3128	2.3555	-2.9240
26	H	1.0751	-1.3729	-2.4586	83	H	2.0673	1.7301	-2.9030
27	H	-0.3238	-3.0474	-3.0578	84	H	0.0795	1.2637	-4.0023
28	O	-4.0978	4.2879	-1.2229	85	O	-0.8250	2.7092	3.8254
29	H	-2.4828	4.7553	-1.1323	86	H	-0.3661	3.2352	4.4885
30	H	-4.1622	3.3041	-1.2750	87	H	-2.4995	3.1405	3.3144
31	O	-3.0656	0.8551	1.3834	88	O	-0.3604	0.4444	-4.2855
32	H	-1.5281	0.0794	0.4631	89	H	0.5001	-0.9567	-3.8465
33	H	-3.2785	1.6884	1.8660	90	H	-1.1827	0.3507	-3.7626
34	O	-1.7458	0.0431	3.7616	91	O	-6.1364	-2.1699	-2.5179
35	H	-2.0614	0.2380	2.8558	92	H	-6.8314	-2.1317	-3.1806
36	H	-1.3498	0.8821	4.0644	93	H	-6.2749	-1.4314	-1.8751
37	O	4.6321	-2.8422	-1.1818	94	O	2.4901	0.6100	1.6144
38	H	4.3677	-2.5668	-2.0758	95	H	3.4261	0.9188	1.5697
39	H	3.8245	-3.1138	-0.7078	96	H	2.2737	0.2433	0.7346
40	O	0.6353	2.6365	1.6173	97	O	-4.0781	1.5734	-1.1566
41	H	1.3663	1.9839	1.7143	98	H	-3.5455	1.0714	-1.8157
42	H	-0.2613	2.7079	2.9981	99	H	-3.6274	1.4036	-0.3050

Table 13. (continued) Atomic positions of 38-molecule randomly-distributed water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
43	O	-2.3773	-0.1418	-2.4561	100	O	-1.0577	-0.6196	-0.0231
44	H	-1.8003	-0.2406	-1.6718	101	H	-1.2344	-1.4786	0.4220
46	O	-3.9110	-3.2070	0.5627	103	O	2.5738	4.6021	-1.7675
47	H	-4.3404	-4.0630	0.6635	104	H	1.6917	3.2353	-2.7354
48	H	-4.6919	-1.8166	1.3693	105	H	1.9973	4.8484	-0.9922
49	O	5.8230	-1.3093	0.7090	106	O	1.5424	-0.7273	-0.7135
50	H	5.3628	-0.4518	0.6216	107	H	1.7867	-1.6240	-0.3668
51	H	5.5369	-1.8787	-0.0441	108	H	2.7958	0.1230	-1.7328
52	O	-0.8993	-3.7400	-2.6743	109	O	0.9322	5.1333	0.2683
53	H	-0.2979	-4.3822	-1.3153	110	H	0.0224	5.1695	-0.0779
54	H	-1.8230	-3.4242	-2.6774	111	H	0.9650	4.3791	0.8870
55	O	-4.2917	-0.8703	4.4162	112	O	-1.4985	4.8419	-1.2157
56	H	-3.3586	-0.5723	4.3841	113	H	-0.9511	3.0851	-0.9869
57	H	-4.3823	-1.4927	5.1441	114	H	-1.3305	5.1937	-2.0966

Table 14. Oscillation frequencies and IR intensities for 38-molecule (38H₂O) randomly-distributed water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
18.877	1.673	110.150	0.362	251.997	46.167	486.157	56.523
25.719	2.731	116.171	5.009	254.329	120.773	490.631	28.469
32.402	0.463	122.019	2.853	256.529	24.978	498.247	11.597
33.596	1.840	132.525	4.631	259.791	44.132	499.889	12.302
34.923	0.577	133.259	6.815	262.142	39.332	511.356	25.647
37.556	1.052	138.120	0.981	267.129	26.924	523.575	32.314
42.378	0.209	138.579	5.362	269.968	16.181	529.792	18.046
44.584	0.195	140.518	9.746	278.959	13.898	535.958	23.588
47.214	1.215	144.820	2.537	281.719	4.552	542.993	2.092
48.576	0.835	151.573	5.657	286.854	35.468	554.866	15.079
49.802	3.527	155.924	8.778	289.329	45.639	559.028	30.640
50.676	0.505	158.712	8.073	292.122	6.362	565.209	2.091
53.507	0.429	161.213	0.836	294.717	25.237	570.907	27.807
55.308	0.400	164.404	19.537	296.451	81.030	571.403	8.913
57.675	1.164	166.424	4.595	304.726	22.655	579.287	5.495
61.269	0.488	169.977	3.171	310.369	29.317	583.583	35.758
62.529	3.349	173.198	12.147	313.306	21.849	586.099	2.772
64.459	0.244	177.515	16.204	316.059	23.907	593.200	62.018
65.831	0.912	181.612	3.759	317.594	7.317	599.844	9.764
68.336	0.429	184.905	14.166	319.281	22.848	600.525	41.748
68.765	0.486	190.734	11.625	321.274	25.299	605.594	106.984
70.718	1.127	193.289	81.198	323.467	37.059	618.508	27.129
72.195	1.306	195.236	15.636	324.272	32.605	623.663	62.128
73.839	1.479	200.056	6.925	330.103	4.785	630.732	33.531
74.665	0.865	201.313	22.987	331.696	10.462	632.355	26.462
76.311	0.776	205.072	10.780	335.026	51.256	635.146	2.714
77.098	1.880	206.635	23.498	340.249	8.418	636.684	29.458
78.218	0.395	209.608	13.351	351.017	22.259	644.579	18.671
81.169	0.901	212.803	1.832	356.200	10.780	651.949	107.383
84.648	2.232	214.717	14.512	361.541	51.788	657.304	87.362
85.560	1.257	224.057	12.119	363.126	32.900	661.575	129.767
85.954	0.029	226.274	68.611	365.013	64.080	665.232	54.511
88.677	0.995	227.305	17.007	374.986	55.924	668.220	91.688
91.498	1.852	230.839	23.910	381.790	18.473	680.556	54.643
92.918	0.864	232.147	5.613	398.420	71.623	683.817	38.084
94.075	1.727	233.257	18.042	409.583	58.554	688.093	53.841
96.513	1.500	237.376	9.475	440.364	162.900	707.120	132.560
99.724	0.799	239.124	42.996	459.446	33.585	710.117	109.508
100.519	3.654	242.188	41.692	466.657	83.120	715.055	106.492
103.427	4.613	245.982	50.244	473.038	77.945	721.913	11.626
105.729	2.102	247.081	266.221	476.443	8.703	722.777	56.227
107.855	1.185	250.478	16.188	478.313	67.177	730.142	30.591

Table 14 (continued). Oscillation frequencies and IR intensities for 38-molecule (38H₂O) randomly-distributed water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
734.06	260.46	1054.22	34.11	1807.36	110.13	3519.92	936.15
745.71	41.72	1059.79	101.02	1809.90	157.12	3527.69	455.42
756.19	74.08	1069.64	109.15	1811.40	108.37	3535.77	35.84
758.33	97.46	1077.66	390.67	1814.15	39.11	3540.28	204.63
761.82	45.91	1086.46	152.04	1822.40	116.46	3545.58	323.61
771.13	172.80	1092.24	198.38	1824.97	45.66	3546.18	32.76
774.71	126.06	1103.00	153.87	1827.95	74.58	3553.16	768.51
789.02	188.22	1116.85	79.33	1849.71	56.18	3561.34	354.04
792.04	402.52	1142.58	38.21	3022.21	949.92	3564.92	378.28
798.09	538.75	1160.20	174.44	3080.30	1466.41	3567.39	1793.14
803.51	210.54	1168.11	320.50	3104.21	1381.31	3568.09	150.23
808.96	200.18	1217.60	57.91	3170.91	789.88	3576.91	163.00
813.85	36.14	1697.90	195.70	3207.15	762.33	3577.63	27.83
820.34	109.85	1698.26	92.60	3225.68	315.11	3582.94	96.34
825.75	36.34	1712.65	51.08	3234.16	822.76	3584.84	275.90
829.16	70.70	1722.71	189.54	3258.12	1941.42	3586.23	145.82
837.26	241.43	1726.51	65.61	3262.36	370.87	3588.62	999.33
839.09	360.72	1728.70	130.78	3273.65	180.55	3598.68	488.37
843.86	13.43	1729.40	190.37	3299.68	981.42	3602.61	239.17
854.97	24.91	1730.39	33.88	3314.10	1099.49	3606.77	624.50
871.73	417.85	1732.43	111.32	3316.46	508.24	3615.36	262.83
875.99	438.53	1733.98	114.28	3321.95	154.85	3625.50	330.69
883.15	11.94	1739.04	38.07	3337.47	448.12	3629.33	291.78
890.44	33.28	1745.43	65.54	3357.84	680.76	3643.10	583.55
903.78	42.30	1748.76	74.48	3370.10	534.82	3652.71	428.65
906.14	366.75	1753.72	101.26	3374.32	1717.16	3654.26	572.99
913.92	226.21	1755.60	120.68	3393.95	1222.93	3672.22	376.78
919.64	73.07	1760.21	116.43	3407.39	953.36	3681.82	516.02
926.54	413.80	1763.03	29.06	3416.91	180.96	3682.03	398.71
936.59	560.61	1764.27	22.36	3428.05	925.25	3691.08	310.21
942.11	124.92	1766.79	26.43	3429.85	448.63	3841.76	47.71
961.48	268.13	1767.15	65.61	3445.51	586.09	3845.17	49.97
968.69	6.78	1767.88	88.75	3452.63	1451.51	3847.71	46.92
969.41	251.03	1771.00	91.31	3462.55	1011.49	3848.56	55.27
976.13	206.93	1781.01	59.32	3475.12	517.50	3853.87	64.28
982.52	148.00	1784.08	10.86	3483.08	251.05	3854.54	47.70
991.02	345.15	1789.09	120.14	3489.94	621.43	3854.86	59.74
1002.38	51.19	1792.61	118.89	3495.60	656.64	3857.22	46.67
1023.70	97.08	1793.76	27.75	3497.00	233.57	3860.62	67.30
1035.43	65.12	1797.61	98.56	3504.00	431.39	3861.18	54.08
1039.48	129.46	1801.10	20.22	3508.44	578.60	3862.28	64.92
1046.34	65.74	1802.81	184.22	3515.37	401.92	3868.93	45.90

Table 15. Excitation energies and oscillator strengths for 38-molecule (38H₂O) randomly-distributed water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital Symmetry	Excitation Energy	Oscillator Strength
Triplet-A	180.12 nm	0.0000
Triplet-A	178.91 nm	0.0000
Triplet-A	178.35 nm	0.0000
Singlet-A	178.28 nm	0.0108
Singlet-A	178.05 nm	0.0104
Singlet-A	176.55 nm	0.0065

Table 16. Atomic positions of five-molecule liquid-phase water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	1.8032	1.4062	-0.0010	9	H	-1.7267	-0.8800	-0.0750
2	H	2.2827	2.0121	-0.5731	10	O	-0.6469	-2.1834	0.1603
3	H	0.8702	1.7229	0.0622	11	H	-0.7259	-2.7157	0.9576
4	O	-0.7864	2.1435	0.1398	12	H	0.2977	-1.9093	0.0775
5	H	-1.1152	2.5971	0.9217	13	O	1.8935	-1.3027	-0.0304
6	H	-1.3748	1.3673	-0.0213	14	H	2.4867	-1.6191	-0.7178
7	O	-2.2760	-0.0722	-0.2193	15	H	1.9401	-0.3180	-0.0181
8	H	-2.8085	-0.2154	-1.0072					

Table 17. Oscillation frequencies and IR intensities for five-molecule (5H₂O) liquid-phase water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
33.85	4.01	282.80	349.85	890.69	336.19	3356.66	2144.61
49.95	0.02	324.54	56.59	941.25	258.73	3368.18	1943.80
76.55	0.58	330.60	12.56	970.00	292.70	3409.62	98.08
83.57	1.82	332.81	3.38	1086.39	26.65	3422.68	107.04
172.19	3.12	445.16	50.30	1721.15	127.38	3858.03	47.25
199.27	119.05	460.25	15.73	1728.20	35.47	3858.60	47.72
206.85	0.62	489.03	12.48	1742.79	121.19	3860.99	50.03
239.05	204.22	505.47	25.94	1758.71	78.73	3862.33	45.79
262.42	2.08	591.99	76.46	1776.26	23.87	3865.00	50.97
265.74	73.01	784.03	55.12	3275.08	38.49		

Table 18. Excitation energies and oscillator strengths for five-molecule (5H₂O) liquid-phase water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital Symmetry	Excitation Energy	Oscillator Strength
Triplet-A	172.24 nm	0.0000
Triplet-A	167.87 nm	0.0000
Triplet-A	167.51 nm	0.0000
Singlet-A	166.90 nm	0.0244
Singlet-A	166.45 nm	0.0363
Singlet-A	163.09 nm	0.0604

Table 19. Atomic positions of twelve-molecule (12H₂O) liquid-phase water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	2.8572	-1.0202	-1.7215	19	O	-2.8573	1.7215	-1.0202
2	H	2.9046	-1.3715	-0.7903	20	H	-2.9046	0.7903	-1.3715
3	H	3.5366	-1.4533	-2.2480	21	H	-3.5369	2.2479	-1.4531
4	O	2.7433	-1.6880	0.8570	22	O	-2.7433	-0.8571	-1.6880
5	H	1.8295	-1.9668	1.0459	23	H	-2.8844	-1.3314	-0.8475
6	H	2.8844	-0.8476	1.3314	24	H	-1.8296	-1.0461	-1.9668
7	O	0.0662	-0.8245	-1.7593	25	O	-2.8573	-1.7215	1.0203
8	H	0.0636	0.1358	-1.5427	26	H	-2.9046	-0.7903	1.3716
9	H	0.9743	-1.0408	-2.0407	27	H	-3.5367	-2.2479	1.4533
10	O	-0.0663	-1.7592	0.8244	28	O	-2.7432	0.8570	1.6881
11	H	-0.0638	-1.5425	-0.1359	29	H	-1.8294	1.0459	1.9668
12	H	-0.9742	-2.0408	1.0409	30	H	-2.8844	1.3314	0.8476
13	O	0.0663	0.8244	1.7591	31	O	2.8573	1.0202	1.7215
14	H	0.0639	-0.1358	1.5424	32	H	2.9046	1.3715	0.7902
15	H	0.9742	1.0410	2.0408	33	H	3.5368	1.4533	2.2479
16	O	-0.0662	1.7592	-0.8245	34	O	2.7433	1.6881	-0.8571
17	H	-0.0639	1.5425	0.1358	35	H	2.8844	0.8476	-1.3314
18	H	-0.9742	2.0410	-1.0410	36	H	1.8295	1.9668	-1.0459

Table 20. Oscillation frequencies and IR intensities for twelve-molecule ($12\text{H}_2\text{O}$) liquid-phase water cluster after geometry optimization.

Frequency cm^{-1}	Intensity KM/Mol	Frequency cm^{-1}	Intensity KM/Mol	Frequency cm^{-1}	Intensity KM/Mol	Frequency cm^{-1}	Intensity KM/Mol
63.238	0.089	291.300	0.000	778.81	854.22	3162.41	0.00
69.880	0.385	293.892	1.545	786.73	29.90	3164.71	11.02
69.881	0.385	307.631	73.426	786.77	30.08	3202.80	1364.63
86.327	2.492	307.639	73.434	800.29	855.96	3202.83	1364.68
86.327	2.491	338.041	69.597	800.31	855.69	3331.76	0.00
96.450	0.000	351.796	0.000	916.13	0.00	3421.21	1168.98
101.825	2.654	361.626	131.913	934.29	260.00	3421.27	1168.68
103.073	0.000	361.634	131.854	934.34	259.88	3459.60	2.77
124.493	3.450	464.301	0.457	980.88	2.98	3581.12	445.93
129.992	0.000	481.720	0.000	1091.46	242.12	3585.10	213.33
138.541	0.000	496.177	36.989	1091.50	242.07	3585.11	212.46
146.069	0.274	496.184	36.961	1165.31	0.00	3585.32	0.13
146.071	0.274	543.359	13.809	1185.97	122.05	3612.30	0.03
173.411	8.440	554.958	0.000	1200.41	0.00	3617.05	243.80
188.851	0.000	566.022	7.417	1703.65	113.52	3617.12	243.76
190.775	8.281	566.025	7.398	1703.66	113.50	3620.45	903.44
192.923	2.155	570.978	0.000	1711.88	418.57	3664.29	1295.08
192.936	2.156	589.834	4.968	1715.65	0.00	3665.36	435.74
225.809	0.000	605.911	106.041	1749.14	78.33	3665.38	435.83
231.169	0.576	605.932	105.942	1749.15	78.40	3671.65	0.01
236.520	6.708	624.063	25.583	1751.51	0.00	3853.00	68.64
236.534	6.706	713.263	0.000	1768.35	315.30	3853.00	68.66
275.209	0.000	747.322	0.003	1802.51	9.75	3853.10	44.47
278.722	0.683	749.767	43.470	1802.52	9.74	3853.17	0.06
282.028	15.040	751.647	54.014	1803.46	18.99		
282.039	15.040	751.667	53.705	1829.03	0.00		

Table 21. Excitation energies and oscillator strengths for 12-molecule ($12\text{H}_2\text{O}$) liquid-phase water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital Symmetry	Excitation Energy	Oscillator Strength
Triplet-A	168.99 nm	0.0000
Triplet-A	168.78 nm	0.0000
Triplet-A	168.78 nm	0.0000
Singlet-A	164.48 nm	0.0678
Singlet-A	164.11 nm	0.0751
Singlet-A	163.93 nm	0.0752

Table 22. Atomic positions of 24-molecule liquid-phase water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	-6.9217	1.5096	-1.1310	37	O	1.3273	1.1291	1.6067
2	H	-6.0103	1.7550	-1.3707	38	H	0.4308	1.3846	1.8908
3	H	-7.0625	0.6006	-1.4549	39	H	1.3372	0.1470	1.5627
4	O	-4.1136	1.5945	-1.1247	40	O	-4.1136	-1.5945	1.1247
5	H	-3.2277	1.8960	-1.3944	41	H	-3.2277	-1.8960	1.3944
6	H	-4.1075	1.5475	-0.1420	42	H	-4.1075	-1.5475	0.1420
7	O	-1.3328	1.5191	-1.2438	43	O	-1.3328	-1.5191	1.2438
8	H	-0.4365	1.8420	-1.4494	44	H	-0.4365	-1.8420	1.4494
9	H	-1.3427	0.5612	-1.4650	45	H	-1.3427	-0.5612	1.4650
10	O	1.4476	1.6065	-1.1247	46	O	1.4476	-1.6065	1.1247
11	H	1.4421	1.5607	-0.1421	47	H	1.4421	-1.5607	0.1421
12	H	2.3426	1.8919	-1.3837	48	H	2.3426	-1.8919	1.3837
13	O	-7.0177	-1.3078	-1.5244	49	O	4.2284	-1.5065	1.2335
14	H	-7.0745	-1.4912	-0.5467	50	H	4.2148	-0.5466	1.4519
15	H	-7.6919	-1.8268	-1.9742	51	H	5.1413	-1.8077	1.4005
16	O	-4.2307	-1.1212	-1.5978	52	O	4.1116	1.2413	1.5056
17	H	-5.1440	-1.3747	-1.8295	53	H	3.2277	1.4601	1.8506
18	H	-4.2196	-0.1382	-1.5548	54	H	4.1014	1.4593	0.5459
19	H	-2.3459	-1.4515	-1.8417	55	O	4.1116	-1.2413	-1.5056
20	O	-1.4507	-1.2451	-1.5164	56	H	3.2277	-1.4601	-1.8506
21	H	-1.4441	-1.4654	-0.5579	57	H	4.1014	-1.4593	-0.5459
22	H	0.4308	-1.3846	-1.8908	58	O	4.2284	1.5065	-1.2335
23	O	1.3273	-1.1291	-1.6067	59	H	4.2148	0.5466	-1.4519
24	H	1.3372	-0.1470	-1.5627	60	H	5.1413	1.8077	-1.4005
25	O	-7.0177	1.3078	1.5244	61	O	7.0290	1.5626	-1.2615
26	H	-7.0745	1.4912	0.5467	62	H	7.7003	2.0324	-1.7666
27	H	-7.6919	1.8268	1.9742	63	H	7.0957	0.5905	-1.4707
28	H	-7.0625	-0.6006	1.4549	64	O	6.9234	-1.0808	-1.5439
29	O	-6.9217	-1.5096	1.1310	65	H	7.0602	-1.4366	-0.6459
30	H	-6.0103	-1.7550	1.3707	66	H	6.0115	-1.3101	-1.7974
31	O	-4.2307	1.1212	1.5978	67	O	6.9234	1.0808	1.5439
32	H	-5.1440	1.3747	1.8295	68	H	7.0602	1.4366	0.6459
33	H	-4.2196	0.1382	1.5548	69	H	6.0115	1.3101	1.7974
34	O	-1.4507	1.2451	1.5164	70	H	7.0957	-0.5905	1.4707
35	H	-2.3459	1.4515	1.8417	71	O	7.0290	-1.5626	1.2615
36	H	-1.4441	1.4654	0.5579	72	H	7.7003	-2.0324	1.7666

Table 23. Oscillation frequencies and IR intensities for 24-molecule liquid-phase water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
28.066	0.043	199.373	0.003	362.151	51.108	745.069	64.416
28.862	0.056	203.140	1.660	369.683	114.903	748.681	94.729
32.759	0.021	204.038	2.416	477.287	0.383	749.136	193.046
50.705	0.027	210.043	0.716	481.274	0.588	753.250	44.567
51.602	0.036	213.204	0.549	495.238	30.378	757.988	59.641
63.104	0.140	213.963	0.039	495.598	70.666	759.499	27.045
67.481	0.009	213.985	0.022	514.748	0.891	766.685	1.982
69.580	0.106	217.620	0.032	524.961	3.288	783.868	725.729
73.243	0.053	218.970	0.057	530.915	24.477	785.131	108.545
80.806	0.824	220.360	0.000	534.704	18.443	793.408	89.637
83.081	1.516	223.536	0.198	539.155	0.777	797.213	167.154
87.355	1.388	224.168	5.766	546.030	3.873	804.149	376.969
87.860	1.286	231.026	3.435	548.926	4.893	809.014	970.970
89.942	1.691	241.228	2.752	551.915	27.788	812.147	944.232
100.476	0.832	261.151	0.245	553.414	4.478	825.049	1441.708
102.239	9.547	261.463	10.727	559.764	14.346	877.463	4.586
104.001	0.004	263.832	0.070	570.395	0.311	882.520	45.284
104.509	0.366	265.864	39.603	571.927	26.191	885.855	60.716
105.088	0.002	267.057	26.179	585.169	0.041	902.129	12.184
105.786	0.061	269.488	90.744	588.235	29.964	911.058	6.528
112.988	0.001	276.254	0.383	604.155	2.451	920.843	196.357
119.155	0.185	280.651	0.091	617.467	30.664	938.406	159.856
125.201	5.147	280.691	37.527	617.713	1.711	945.402	0.490
129.228	0.083	283.815	43.375	622.829	32.834	979.729	2.730
137.621	0.069	292.351	0.082	634.285	16.087	979.762	12.410
141.452	0.137	296.289	0.346	642.670	68.188	994.505	595.509
143.390	10.265	300.657	0.042	644.989	5.364	996.197	855.201
147.460	0.564	302.312	8.523	646.551	150.190	1011.102	0.001
149.743	0.308	303.914	12.682	659.737	0.697	1061.985	237.792
177.866	0.001	308.512	0.003	683.468	9.431	1094.217	244.183
182.687	0.028	310.921	98.253	713.920	133.762	1101.571	2.154
185.198	0.412	313.466	49.497	714.570	52.432	1134.568	1.977
185.989	0.380	347.885	43.585	725.044	0.642	1167.970	7.131
186.923	0.726	355.333	40.458	737.448	28.287	1177.414	138.757

Table 23 (continued). Oscillation frequencies and IR intensities for 24-molecule liquid-phase water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
1188.172	1.642	1798.838	29.354	3431.364	39.467	3631.928	830.823
1196.141	38.714	1800.679	0.322	3443.514	9.032	3637.636	71.231
1701.564	105.629	1805.572	3.049	3454.979	1.043	3640.539	2849.033
1703.005	121.129	1807.036	31.427	3460.250	2.695	3643.657	43.974
1709.219	450.330	1808.088	9.534	3461.944	2894.592	3651.429	127.453
1713.129	211.065	1824.022	45.729	3466.969	3034.589	3654.451	193.301
1732.777	187.621	1833.468	14.860	3474.788	0.067	3656.191	535.634
1737.404	176.892	3160.694	3.751	3491.566	98.879	3657.618	0.565
1738.220	20.906	3164.466	3.632	3582.141	1048.763	3664.036	369.411
1743.878	2.058	3199.703	1317.897	3582.661	184.397	3667.091	18.142
1750.818	784.679	3203.454	1318.099	3583.091	109.411	3669.384	373.151
1753.739	7.173	3336.688	0.161	3583.609	125.657	3672.359	96.843
1756.117	442.777	3344.777	0.320	3602.234	1599.471	3672.765	16.028
1765.997	47.498	3359.519	0.001	3605.041	106.265	3851.803	68.638
1775.687	49.109	3362.013	0.005	3605.899	396.669	3851.953	22.840
1789.729	10.792	3410.743	77.120	3608.204	446.973	3852.660	69.818
1790.245	1.245	3411.803	100.284	3617.962	0.239	3852.794	22.454
1796.297	28.808	3414.821	248.949	3620.453	167.443		
1796.513	8.245	3419.356	408.467	3624.967	150.329		

Table 24. Excitation energies and oscillator strengths for twenty four-molecule (24H₂O) liquid-phase water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital symmetry	Excitation Energy	Oscillator Strength
Triplet-B	169.32 nm	0.0000
Triplet-B	169.30 nm	0.0000
Triplet-A	168.54 nm	0.0000
Singlet-B	167.77 nm	0.0448
Singlet-B	166.12 nm	0.0721
Singlet-A	164.60 nm	0.1241

Table 25. Atomic positions of 38-molecule liquid-phase water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
1	O	11.836	-1.023	-1.346	58	O	0.698	-1.477	-1.443
2	H	10.935	-1.271	-1.620	59	H	0.655	-0.498	-1.524
3	H	11.934	-0.071	-1.534	60	H	-0.184	-1.813	-1.688
4	O	9.034	-1.223	-1.352	61	O	-2.091	-1.591	-1.446
5	H	8.160	-1.517	-1.664	62	H	-2.970	-1.927	-1.699
6	H	9.032	-1.323	-0.373	63	H	-2.140	-0.610	-1.514
7	O	6.252	-1.242	-1.459	64	O	-4.864	-1.813	-1.344
8	H	5.369	-1.569	-1.710	65	H	-5.747	-2.093	-1.644
9	H	6.218	-0.262	-1.533	66	H	-4.857	-1.913	-0.365
10	O	3.481	-1.464	-1.349	67	O	-7.648	-1.792	-1.451
11	H	3.491	-1.568	-0.371	68	H	-8.554	-2.086	-1.661
12	H	2.597	-1.745	-1.648	69	H	-7.661	-0.811	-1.512
13	O	11.805	1.822	-1.324	70	O	-10.447	-1.949	-1.388
14	H	11.863	1.862	-0.330	71	H	-10.498	-2.018	-0.391
15	H	12.455	2.428	-1.694	72	H	-11.113	-2.530	-1.769
16	O	9.027	1.536	-1.418	73	O	-2.094	1.174	-1.303
17	H	9.927	1.859	-1.612	74	H	-2.095	1.255	-0.322
18	H	9.058	0.558	-1.520	75	H	-1.211	1.458	-1.602
19	H	7.130	1.823	-1.603	76	O	-4.868	0.967	-1.415
20	O	6.246	1.535	-1.310	77	H	-3.984	1.301	-1.654
21	H	6.241	1.606	-0.329	78	H	-4.833	-0.011	-1.514
22	H	4.356	1.650	-1.658	79	H	-6.759	1.263	-1.586
23	O	3.474	1.314	-1.416	80	O	-7.639	0.973	-1.284
24	H	3.511	0.336	-1.518	81	H	-7.634	1.034	-0.299
25	O	11.937	-1.205	1.310	82	H	-9.447	1.052	-1.648
26	H	11.995	-1.241	0.316	83	O	-10.388	0.850	-1.473
27	H	12.636	-1.754	1.679	84	H	-10.510	-0.110	-1.623
28	H	11.906	0.692	1.521	85	O	-1.970	-1.724	1.326
29	O	11.727	1.632	1.332	86	H	-1.966	-1.806	0.345
30	H	10.810	1.804	1.609	87	H	-1.067	-1.934	1.624
31	O	9.145	-1.154	1.412	88	H	-2.165	0.050	1.536
32	H	10.069	-1.400	1.603	89	O	-2.196	1.031	1.467
33	H	9.094	-0.176	1.515	90	H	-3.099	1.295	1.724
34	O	6.373	-1.387	1.311	91	O	-4.757	-1.745	1.425
35	H	7.278	-1.599	1.602	92	H	-3.852	-2.006	1.672
36	H	6.371	-1.458	0.330	93	H	-4.805	-0.769	1.534
37	O	3.592	-1.399	1.425	94	O	-7.544	-1.943	1.320
38	H	4.500	-1.660	1.665	95	H	-6.653	-2.180	1.630
39	H	3.546	-0.422	1.528	96	H	-7.529	-2.018	0.340
40	O	8.919	1.596	1.346	97	O	-10.371	-1.877	1.259
41	H	8.024	1.816	1.661	98	H	-9.470	-2.096	1.553
42	H	8.905	1.695	0.367	99	H	-10.526	-0.940	1.494

Table 25 (continued) Atomic positions of 38-molecule liquid-phase water cluster after geometry optimization.

Center Number	Atomic Type	Coordinates (Å)			Center Number	Atomic Type	Coordinates (Å)		
		X	Y	Z			X	Y	Z
44	H	5.239	1.633	1.716	101	H	-5.880	1.232	1.668
45	H	6.194	0.402	1.535	102	H	-4.975	1.130	0.393
46	O	3.365	1.369	1.360	103	O	-7.735	0.817	1.458
47	H	3.364	1.474	0.382	104	H	-8.658	1.070	1.666
48	H	2.462	1.575	1.662	105	H	-7.697	-0.162	1.540
49	O	0.591	1.148	1.459	106	O	-10.475	0.912	1.354
50	H	0.630	0.169	1.541	107	H	-10.486	0.962	0.377
51	H	-0.315	1.410	1.707	108	H	-11.207	1.496	1.650
52	O	0.819	-1.615	1.320	109	O	-12.603	2.622	1.483
53	H	1.720	-1.834	1.619	110	H	-13.479	2.443	1.837
54	H	0.829	-1.684	0.338	111	H	-12.682	2.730	0.510
55	O	0.694	1.295	-1.303	112	O	-12.482	2.618	-1.251
56	H	1.573	1.589	-1.604	113	H	-11.744	2.016	-1.483
57	H	0.700	1.364	-0.321	114	H	-12.448	3.376	-1.841

Table 26. Oscillation frequencies and IR intensities for 38-molecule liquid-phase water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
12.667	0.033	136.691	0.176	262.709	48.849	538.404	2.452
13.573	0.061	138.989	0.004	263.345	10.118	543.438	9.870
20.272	0.132	144.949	0.518	264.683	15.133	545.604	0.926
22.676	0.109	145.747	0.878	265.187	13.024	549.883	8.168
29.271	0.435	148.807	1.468	266.677	21.084	554.364	10.035
33.708	0.112	150.930	0.233	269.188	71.689	555.431	1.564
39.343	0.013	169.090	0.059	269.466	51.289	559.876	7.640
41.914	2.096	173.499	4.447	269.809	113.728	560.552	4.605
44.831	0.048	176.157	6.566	271.218	52.905	565.676	17.523
49.067	0.931	176.574	0.519	275.361	2.771	571.635	31.891
49.878	0.105	186.588	6.285	278.227	17.736	573.575	8.544
56.657	1.106	189.046	6.227	280.947	29.017	580.782	4.801
62.333	0.351	193.266	6.178	282.217	23.086	585.668	11.375
63.420	0.481	194.307	24.331	288.443	0.508	588.919	10.211
71.925	0.814	201.420	72.272	293.949	9.942	593.206	16.493
73.307	0.143	203.959	18.703	294.844	6.735	599.401	9.608
76.288	0.787	206.764	0.231	295.789	5.126	606.363	1.941
78.364	1.396	207.331	17.620	299.913	2.777	613.519	10.848
82.600	0.441	209.301	0.487	302.794	0.535	616.459	21.317
84.709	0.372	210.701	2.915	307.577	36.174	620.401	27.918
86.065	0.479	212.528	0.270	308.291	9.280	625.224	58.641
86.873	0.920	213.741	1.133	311.448	44.655	628.565	6.492
88.499	0.572	214.350	0.081	312.851	77.823	633.070	103.019
90.211	0.078	214.390	0.284	314.093	1.471	634.786	13.939
90.995	0.226	215.292	0.502	318.752	5.597	640.756	2.255
92.983	0.136	216.416	2.625	335.525	11.308	648.649	1.817
94.707	2.021	217.071	0.617	347.387	37.116	654.441	19.405
97.445	3.868	218.184	0.624	365.163	114.979	661.466	136.541
101.249	0.698	219.476	1.613	381.245	45.902	661.676	122.427
101.962	2.862	219.796	0.363	452.585	69.969	669.502	0.675
105.073	1.422	220.491	0.380	458.427	57.132	682.102	23.272
107.031	1.787	220.691	1.227	473.934	0.394	704.436	52.428
107.349	2.412	222.219	2.162	486.697	6.709	718.429	72.973
113.144	1.283	222.595	2.912	489.945	30.572	723.132	9.927
114.711	0.584	228.718	5.624	496.624	8.798	728.898	26.467
114.952	0.779	230.682	3.554	510.007	8.653	733.650	10.381
118.114	1.837	251.279	5.739	511.214	6.693	734.443	16.513
120.661	0.037	254.771	20.862	514.934	1.050	737.272	44.894
122.068	0.011	256.955	3.667	519.797	14.782	740.532	58.350
124.978	7.637	257.835	4.736	528.083	3.688	744.804	50.643
128.318	1.651	260.634	6.258	529.348	14.812	746.231	134.490
134.989	6.622	261.272	42.749	534.580	10.267	747.725	135.052

Table 26 (continued). Oscillation frequencies and IR intensities for 38-molecule liquid-phase water cluster after geometry optimization.

Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol	Frequency cm ⁻¹	Intensity KM/Mol
750.38	70.83	1014.66	9.75	1804.43	1.54	3507.37	470.22
752.67	51.93	1051.28	225.56	1806.38	18.77	3514.24	741.60
753.42	135.83	1095.37	250.53	1808.20	1.33	3555.24	276.25
754.88	90.07	1101.99	4.63	1809.20	4.17	3565.26	530.90
759.75	102.53	1110.22	8.34	1812.86	17.07	3579.42	231.34
764.34	4.23	1131.16	1.48	1822.04	56.98	3580.64	115.61
775.18	76.77	1150.31	32.67	1829.81	3.70	3581.03	707.70
780.51	317.63	1164.76	10.00	1834.76	6.05	3600.20	1720.26
785.04	40.49	1177.15	53.57	3107.28	714.61	3603.43	476.83
786.81	388.77	1184.58	10.41	3160.73	3.57	3606.66	354.54
788.26	237.21	1193.82	46.73	3200.17	1323.06	3609.71	150.99
798.24	485.58	1196.46	12.85	3328.55	118.00	3612.10	1117.09
800.69	578.25	1703.64	120.04	3344.12	0.31	3613.81	564.92
804.04	167.74	1713.28	110.25	3349.97	0.29	3614.93	2255.38
806.38	640.23	1713.79	339.17	3350.59	0.84	3618.45	366.52
813.18	1305.75	1717.01	300.24	3359.74	0.01	3621.61	440.03
821.06	1186.48	1729.43	108.12	3360.47	6.03	3626.92	1634.88
828.17	591.80	1732.69	249.22	3362.07	0.00	3628.22	342.56
850.45	133.75	1734.59	306.22	3409.67	57.99	3630.97	1108.52
852.62	533.39	1737.36	18.91	3411.13	47.82	3635.74	326.68
883.93	221.49	1739.33	64.86	3411.36	20.52	3637.63	54.67
885.21	50.04	1740.46	20.87	3413.78	91.83	3639.97	21.18
885.67	36.42	1741.26	892.09	3415.87	49.97	3642.95	29.09
892.35	196.89	1745.08	97.76	3420.13	64.65	3643.84	77.80
895.03	85.88	1746.88	1360.74	3424.65	142.92	3645.26	17.46
903.51	25.64	1752.27	68.57	3428.37	31.76	3649.12	112.32
906.12	469.91	1754.65	26.20	3432.22	136.35	3651.79	240.97
908.06	17.64	1755.56	133.72	3437.66	276.12	3652.95	195.92
918.18	43.66	1758.89	45.92	3446.08	97.02	3655.15	470.75
924.35	162.70	1764.14	169.98	3451.56	43.78	3656.31	163.01
933.06	13.51	1766.49	145.59	3455.62	4.30	3657.06	53.47
934.80	75.75	1777.33	5.24	3459.24	23.11	3660.54	32.99
935.21	31.14	1778.42	11.97	3459.39	67.16	3663.81	210.46
945.72	2.66	1787.83	10.85	3463.84	1054.43	3665.86	35.16
977.44	9.04	1790.22	2.67	3465.86	1527.02	3668.24	361.14
983.93	38.39	1792.41	2.65	3469.20	1015.52	3671.17	64.29
984.27	16.49	1795.46	0.48	3471.16	4792.21	3675.92	80.23
990.24	2.62	1797.62	3.07	3476.04	1624.44	3850.36	45.59
992.17	160.54	1798.44	3.65	3478.93	684.94	3851.95	63.99
997.60	961.98	1800.04	2.42	3488.46	435.93	3852.14	28.90
1001.57	1478.44	1801.70	0.51	3491.86	1032.23	3859.24	52.98
1005.92	166.37	1804.15	30.18	3494.69	163.69	3862.93	65.64

Table 27. Excitation energies and oscillator strengths for 38-molecule (38H₂O) liquid-phase water cluster after geometry optimization calculated using TD-DFT.

Multiplicity-Orbital Symmetry	Excitation Energy	Oscillator Strength
Triplet-A	171.24 nm	0.0000
Triplet-A	169.85 nm	0.0000
Triplet-A	169.36 nm	0.0000
Singlet-A	168.58 nm	0.0635
Singlet-A	167.58 nm	0.0329
Singlet-A	166.54 nm	0.0703

Table 28. Denumeration of critical points associated with electron density and calculated bond paths for randomly distributed water molecules comprising a cluster. Bond critical point (BCP), ring critical point (RCP) and cage critical point (CCP).

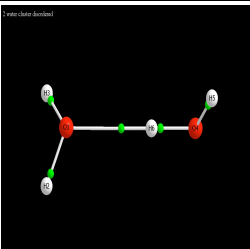
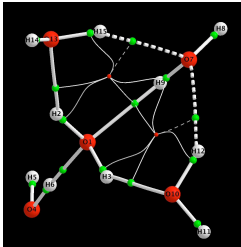
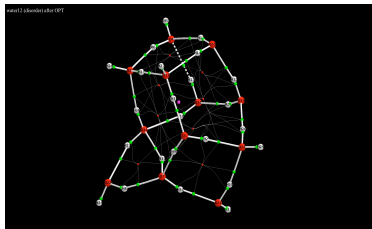
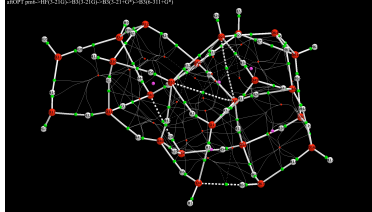
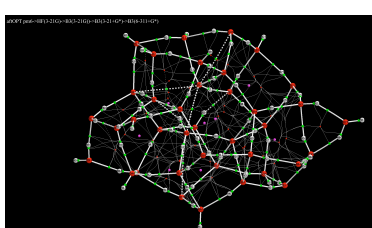
	Randomly Distributed Water	BCP	RCP	CCP
2 H ₂ O		5	0	0
5 H ₂ O		16	2	0
12 H ₂ O		42	8	1
24 H ₂ O		91	26	6
38 H ₂ O		145	40	8

Table 29. Denumeration of critical points associated with electron density and calculated bond paths for liquid water comprising a cluster. Bond critical point (BCP), ring critical point (RCP) and cage critical point (CCP).

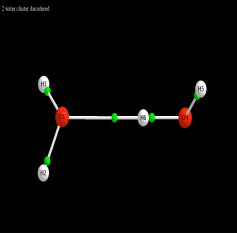
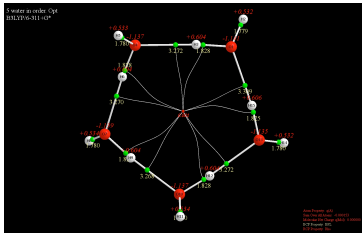
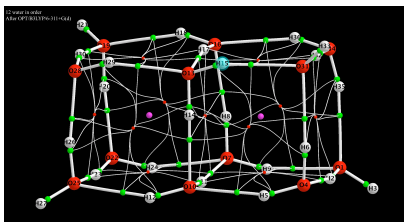
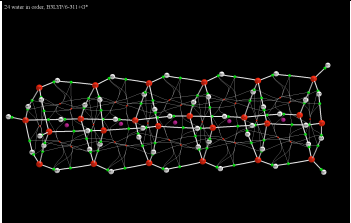
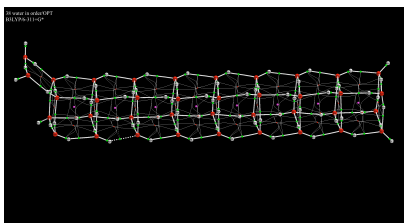
	Liquid Water	BCP	RCP	CCP
2 H ₂ O		5	0	0
5 H ₂ O		15	1	0
12 H ₂ O		44	11	2
24 H ₂ O		92	26	5
38 H ₂ O		147	42	8

Table 30. AIMQB Net Charge of Atoms

	Randomly Distributed					Liquid Phase			
Atom	2 H ₂ O	5 H ₂ O	12 H ₂ O	24 H ₂ O	38 H ₂ O	5 H ₂ O	12 H ₂ O	24 H ₂ O	38 H ₂ O
O1	-1.0671	-1.1458	-1.1677	-1.1657	-1.2058	-1.1408	-1.1536	-1.1469	-1.1467
H2	0.5442	0.5843	0.5855	0.5826	0.6085	0.5323	0.6031	0.5822	0.5821
H3	0.5447	0.5841	0.6164	0.5885	0.6106	0.6042	0.5423	0.5781	0.5783
O4	-1.1010	-1.1063	-1.1293	-1.1373	-1.1863	-1.1368	-1.1469	-1.1723	-1.1721
H5	0.5121	0.5068	0.5429	0.5441	0.5964	0.5335	0.5821	0.5885	0.5884
H6	0.5672	0.5728	0.5902	0.5999	0.5944	0.6041	0.5783	0.5840	0.5839
O7		-1.1324	-1.1719	-1.1530	-1.1228	-1.1391	-1.1765	-1.1737	-1.1733
H8		0.5428	0.5843	0.6074	0.5403	0.5341	0.5848	0.5893	0.5892
H9		0.5843	0.5866	0.5420	0.5402	0.6041	0.5862	0.5836	0.5835
O10		-1.1068	-1.1386	-1.1498	-1.1667	-1.1372	-1.1765	-1.1742	-1.1738
H11		0.5391	0.5679	0.6032	0.5798	0.5341	0.5846	0.5843	0.5841
H12		0.5716	0.5873	0.5445	0.5914	0.6045	0.5863	0.5894	0.5895
O13		-1.1024	-1.1581	-1.1358	-1.1809	-1.1351	-1.1766	-1.1538	-1.1539
H14		0.5382	0.5683	0.6013	0.5942	0.5321	0.5848	0.6034	0.6034
H15		0.5695	0.6080	0.5369	0.5948	0.6059	0.5863	0.5431	0.5431
O16			-1.1420	-1.1498	-1.1469		-1.1766	-1.1785	-1.1784
H17			0.5652	0.5405	0.5990		0.5848	0.5875	0.5876
H18			0.5780	0.6074	0.5457		0.5862	0.5850	0.5851
O19			-1.1803	-1.1747	-1.1856		-1.1536	0.5897	0.5898
H20			0.6149	0.5885	0.5824		0.6030	-1.1742	-1.1743
H21			0.5909	0.5805	0.6025		0.5423	0.5844	0.5842
O22			-1.1263	-1.1646	-1.1955		-1.1469	0.5893	0.5899
H23			0.5884	0.5798	0.5877		0.5783	-1.1738	-1.1742
H24			0.5345	0.5895	0.6075		0.5821	0.5838	0.5840
O25			-1.1443	-1.1425	-1.1712		-1.1536	-1.1537	-1.1538
H26			0.5459	0.5370	0.5647		0.6030	0.6033	0.6035
H27			0.5428	0.6052	0.5899		0.5423	0.5431	0.5431
O28			-1.1598	-1.1621	-1.1381		-1.1469	0.5784	0.5783
H29			0.5399	0.5786	0.6101		0.5822	-1.1469	-1.1467
H30			0.5934	0.5913	0.6027		0.5784	0.5822	0.5822
O31			-1.1293	-1.1976	-1.2023		-1.1536	-1.1785	-1.1784
H32			0.5961	0.6033	0.5936		0.6030	0.5872	0.5874
H33			0.5350	0.5919	0.5975		0.5423	0.5852	0.5850
O34			-1.1675	-1.1381	-1.1578		-1.1469	-1.1742	-1.1742
H35			0.5730	0.5652	0.5731		0.5784	0.5896	0.5899
H36			0.5801	0.5736	0.5858		0.5817	0.5845	0.5842
O37				-1.1341	-1.1604			-1.1738	-1.1741
H38				0.5997	0.5755			0.5893	0.5899
H39				0.5362	0.5824			0.5837	0.5840
O40				-1.1715	-1.1981			-1.1724	-1.1720
H41				0.5837	0.5953			0.5884	0.5884
H42				0.5915	0.6115			0.5840	0.5839
O43				-1.1730	-1.1697			-1.1737	-1.1733
H44				0.5764	0.5825			0.5894	0.5892
H45				0.5944	0.5884			0.5839	0.5836
O46				-1.1953	-1.1451			-1.1742	-1.1737
H47				0.5936	0.5451			0.5843	0.5841
H48				0.5931	0.5916			0.5894	0.5896
O49				-1.1348	-1.1857			-1.1772	-1.1739

H50				0.5634	0.5740			0.5855	0.5850
H51				0.5773	0.6070			0.5871	0.5898
O52				-1.1889	-1.1746			-1.1729	-1.1738
H53				0.5821	0.6164			0.5877	0.5893
H54				0.5978	0.5907			0.5843	0.5834
O55				-1.1862	-1.1321			-1.1728	-1.1740
H56				0.5882	0.5886			0.5880	0.5894
H57				0.5934	0.5380			0.5843	0.5837
O58				-1.1934	-1.1532			-1.1772	-1.1738
H59				0.5996	0.5740			0.5854	0.5852
H60				0.5968	0.5796			0.5870	0.5896
O61				-1.1554	-1.1591			-1.1530	-1.1740
H62				0.6146	0.5933			0.5424	0.5893
H63				0.5404	0.5464			0.6027	0.5834
O64				-1.1597	-1.1370			-1.1473	-1.1743
H65				0.5858	0.5956			0.5792	0.5890
H66				0.5721	0.5372			0.5823	0.5850
O67				-1.1596	-1.1777			-1.1473	-1.1746
H68				0.5856	0.6022			0.5792	0.5856
H69				0.5715	0.5784			0.5824	0.5830
O70				-1.1237	-1.1694			0.6026	-1.1567
H71				0.5961	0.5819			-1.1530	0.6061
H72				0.5323	0.5965			0.5424	0.5439
O73					-1.1628				-1.1742
H74					0.5388				0.5855
H75					0.5776				0.5895
O76					-1.1705				-1.1742
H77					0.5912				0.5894
H78					0.5828				0.5839
O79					-1.1184				0.5915
H80					0.5808				-1.1785
H81					0.5336				0.5879
O82					-1.1788				0.5952
H83					0.5859				-1.1759
H84					0.5758				0.5907
O85					-1.1562				-1.1732
H86					0.5445				0.5847
H87					0.5910				0.5893
O88					-1.1552				0.5835
H89					0.6020				-1.1746
H90					0.5853				0.5900
O91					-1.1503				-1.1725
H92					0.5345				0.5883
H93					0.6026				0.5838
O94					-1.1736				-1.1689
H95					0.6062				0.5861
H96					0.5708				0.5821
O97					-1.1697				-1.1521
H98					0.5952				0.5802
H99					0.5750				0.5852
O100					-1.1736				-1.1742
H101					0.5934				0.5916
H102					0.6055				0.5824

O103					-1.1521				-1.1829
H104					0.5834				0.5946
H105					0.6056				0.5835
O106					-1.2099				-1.1799
H107					0.5965				0.5734
H108					0.5880				0.5996
O109					-1.1487				-1.1277
H110					0.5801				0.5331
H111					0.5796				0.5944
O112					-1.1470				-1.1312
H113					0.5766				0.5973
H114					0.5399				0.5369