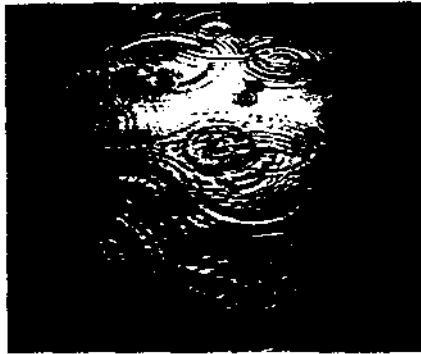


Simulated X-Ray Absorption Spectroscopy on the Water Dimer



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Abstract

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The ability of an individual H₂O molecule to form multiple hydrogen bonds with neighboring molecules makes it an ideal substance for the study of hydrogen bonding. X-ray absorption spectroscopy (XAS) can be used to study what intermolecular structures the hydrogen-bonded water molecules form. XAS excites core electrons from the oxygen 1s atomic orbital to an unoccupied orbital. The resulting absorption spectrum shows the energy levels of the unoccupied orbitals, which in turn is dependent on the intermolecular structure of the H₂O system. Previous studies using molecular dynamics computer simulations have concluded that the intermolecular structure of liquid water is a distorted tetrahedron. Yet x-ray absorption spectra show discrepancies between liquid water and ice Ih, which is already known to have a rigid tetrahedral structure. The research group, which is based in the University of Sweden in Stockholm and the Stanford Synchrotron Radiation Laboratory at the Stanford Linear Accelerator Center, has studied the possible presence of broken hydrogen bonds in the liquid water intermolecular structure to explain these deviations. Computer simulations are used to construct theoretical absorption spectra for models of liquid water including broken hydrogen bonds. Creating such models requires controlling variables. The simplest method of isolating individual variables, such as hydrogen bond length and angles, is to study the water dimer. Here, the water dimer is used to study how the absorption spectra change with the way the water molecules are positioned and oriented relative to each other.

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Introduction

Liquid water is one of the most important and abundant resources on our planet. Yet its molecular structure is strangely elusive to study. It is known that hydrogen bonds (H bonds) can be formed between a hydrogen atom and the lone electron pairs on an oxygen atom of a neighboring water molecule. Since oxygen is more electronegative than hydrogen, the hydrogen atoms have a slight positive charge that attracts them to the lone pairs of oxygen atoms on neighboring H₂O molecules. This attraction is what creates the H bond. That still leaves the question of what intermolecular structure the H-bonded H₂O molecules form. For liquid water, it has been difficult to analyze experimental data that might answer this question.

In contrast to liquid water, interpreting data from X-ray and neutron diffraction on ice is much easier to interpret. This is because ice has a rigid, periodic crystal structure. In particular, the intermolecular structure of ice Ih, a common form of ice as shown in Figure 1, has been successfully analyzed already. Diffraction techniques have discovered that ice Ih forms a rigid tetrahedral arrangement bonded together by H bonds. As shown in Figure 2, the tetrahedron has a central H₂O molecule with four H bonds. Two H bonds connect the hydrogen atoms to oxygen atoms of neighboring molecules. In addition, the oxygen atom of the central H₂O molecule has two more H bonds, connecting the two lone pairs to hydrogen atoms on two neighboring H₂O molecules (Myneni *et al.*, 2002).

Data from diffraction techniques used on liquid water is much more difficult to interpret than for ice. This is partially because of the liquid water's fluidity, unlike the rigid crystal structure of ice. Also, problems arise due to the fact that in liquid water H bonds are constantly broken and reformed. The time scale for this rearrangement is on

the order of a picosecond. Thus, liquid water is composed of many different configurations simultaneously. Experimentalists were able to determine that the average distance is $2.85 \pm 0.5 \text{ \AA}$ between oxygen atoms on neighboring H_2O molecules connected by an H bond (Wilson *et al.*, 2002). However, these experiments were still unable to determine the number of H bonds on each liquid water molecule. Based upon computer simulations, it was concluded that liquid water had a distorted tetrahedral structure, similar to ice Ih (Chaplin, 2002).

Now, with the development of third generation synchrotron radiation laboratories, high-energy radiation is available to begin a new approach to the study of liquid water structure. This research group, which is based at the University of Sweden in Stockholm and at the Stanford Synchrotron Radiation Laboratory, has used X-ray absorption spectroscopy (XAS) to probe the unoccupied molecular orbitals of liquid water. This technique uses X-rays to excite the oxygen 1s core electrons into unoccupied molecular orbitals. Since the presence of H bonds has a strong influence on the energy levels of molecular orbitals, the absorption spectra are dependent on intermolecular structures (Myneni *et al.*, 2002).

The results of such testing have shown that there are notable differences between the absorption spectrum for ice Ih and that of liquid water. This has led to the hypothesis that these differences are a result of a fairly large fraction of liquid water molecules that have broken H bonds. These molecules with broken H bonds would thus not correspond to the distorted tetrahedral structure (Myneni *et al.*, 2002). To test this hypothesis, the group has used Density Functional Theory (DFT) to compute theoretical absorption spectra for different intermolecular structure models containing broken H bonds

(Cavalleri, 2002a). Ultimately, the group would like to create a structure whose theoretical absorption spectrum more closely matches the experimental absorption spectra of liquid water.

It is a challenging task to compute theoretical spectra, considering the many variables that must be controlled and the many intermolecular interactions that must be taken into account. Systems that have been studied with DFT normally contain thirty to forty H₂O molecules, making it even harder to keep track of single variables. This portion of the research instead uses the water dimer, the simplest H bonded configuration. The water dimer consists of two H₂O molecules connected by a H bond. The molecule that contains the hydrogen atom in the H bond will be referred to as the donor molecule, since it has donated positive charge to the bond. Conversely, the molecule that contains the oxygen atom in the H bond is referred to as the acceptor molecule (Myneni *et al.*, 2002). The simplicity of this model makes it more efficient to study the direct effects of changing the molecules' relative positions and orientations.

Ultimately, the study of H₂O intermolecular structure is a study of H bonds. H bonds form the essential building blocks of our universe, binding together water molecules as well as the double helix in our DNA. H bonds explain unique phenomena, such as surface tension and the global water cycle (Wilson *et al.*, 2002). Thus this research has applications in fields such as biology, chemistry, physics, and environmental science. Unlike hydrogen fluoride and other substances that are also capable of forming H bonds, H₂O has the unique property of being able to form multiple H bonds on a single molecule. This fact, as well as its abundance, makes water an ideal substance for the study of H bonds.

Materials and Methods

Calculating the theoretical absorption spectra was preceded by first constructing a model of the water dimer. The first model was the optimized geometry for a water dimer, which had been previously calculated using DFT by the group (Cavalleri, 2002b). Using the graphics program Molden, angles and distances could be systematically varied (Schaftenaar, 2002). Three variables were isolated: the length of the H bond, the O-H...O angle, and the dihedral angle. The dihedral angle is defined to be the angle between the planes of the water molecule. The dihedral angle of the optimal configuration is referred to here as the normal dihedral angle. The length of the H bond is defined as the distance between the center of the oxygen atom and the center of the hydrogen atom within the H bond. For the optimal water dimer geometry, this distance is 1.93 Angstroms. The O-H...O angle is defined as the angle formed by the two oxygen atoms and the hydrogen atom within the H bond. This angle is 171° in the optimal geometry. This angle was varied in two situations: one where the H bond length was kept constant, and one where the O O distance was kept constant. The optimal configuration and these three variables are depicted in Figure 3.

When changing one variable, as many values of the optimized geometry as possible are kept constant. This way, their individual effects are kept isolated from each other. Unfortunately it was not possible to keep the dihedral angle constant while changing the O-H...O angle due to the specifics of Molden. Nonetheless, the effect of this error will be negligible, for reasons explained later. After computing absorption spectra for several different geometric configurations of the water dimer, it is possible to

study the effects of each variable separately. It is also possible to compare and contrast the effects of changing each variable.

With Molden, a set of Cartesian coordinates for the molecules could be generated. The coordinates were inserted into an input file. The computer could then compute absorption spectra from the input file using DFT techniques. Since the absorption spectra contained only discrete impulses of oscillator strength as a function of energy, convolution techniques were used to fit Gaussian curves to each impulse, creating a smooth curve. The convoluted curves more closely simulate experimental spectra, which are affected by finite energy resolution as well as high density of states for certain energy regions. Once the newly convoluted data files had been generated, the graphics program gnuplot (Woo, 2002) was used to plot the absorption spectra for varying distances and angles. For each set of Cartesian coordinates, the absorption spectrum for an excited acceptor molecule was calculated, as well as that of the excited donor molecule.

The computer, using DFT techniques again, can also output the ground state energy (no core hole) of any given geometrical configuration of the water dimer. It is also possible to calculate the ground state energy of each individual water molecule, with the same geometry as the water dimer's acceptor and donor molecule respectively. By subtracting the individual molecules' energies from the total dimer energy, it is possible to calculate the strength, or energy, of the H bond. The H bond strength was thus calculated for several H lengths and O-H...O angles.

Results

Figure 4 shows the absorption spectra calculated for the free H₂O molecule (calculated twice, using the geometry of the acceptor and donor molecules in the

optimized dimer), the acceptor molecule, and the donor molecule in the optimized dimer. Figures 5-9 show the absorption spectra of the acceptor and donor molecules calculated from DFT for varying distances and angles. The primary absorption data are shown as green impulses, scaled vertically by a factor of 5000 in order to be plotted together with the convoluted data. All the spectra have the same scale on the x and y-axis, as shown on the bottom graph of every page. The chosen range of the energy axis focuses on the important near-edge region where most changes in the spectrum are observed.

Figure 5 shows the absorption spectra of the excited acceptor molecule for varying the H bond length and the O-H...O angle for both a constant H bond length and a constant O O distance. Figure 6 shows the absorption spectra of the excited donor molecule for varying the H bond length. Figure 7 shows the donor molecule absorption spectra for varying the O-H...O angle, while maintaining a constant H bond length. Figure 8 shows the same, except the O-H...O angle was varied while the O O distance was kept constant. Figure 9 shows the spectra of the excited acceptor and donor molecule for varying the dihedral angle. Figure 10 shows the calculations of the H bond strength for various geometries.

Discussions and Conclusions

Free v. H bonded molecules

Figure 4 shows the effect of H bonding on the orbital structure of the donor molecule in the water dimer. The two geometries of the free molecule show nearly identical absorption spectra, with two peaks at approximately the same energy levels. While the acceptor molecule shows two strong peaks and some weak additional structure at higher energies like the free molecules, the donor molecule shows a broad band-like intensity around 540 eV. Conceptually, these deviations between the acceptor molecule

and the donor molecule spectra are expected because absorption spectra probe unoccupied orbitals. Since the oxygen lone pairs that participate in the H bond make up occupied orbitals, the presence of an H bond would primarily affect these occupied orbitals. In contrast, the unoccupied antibonding molecular orbitals that form between the oxygen and hydrogen atoms on the donor molecule are affected by the presence of an H bond. Thus the absorption spectrum of the donor molecule should reflect the presence of an H bond, but the spectrum of the acceptor molecule should not (Cavalleri et al., 2002).

This indicates that the absorption spectrum for the acceptor molecule in the optimized dimer will be similar to the absorption spectrum for a free H₂O molecule, which is also unaffected by H bonding. The absorption spectrum of the donor molecule, on the other hand, is not expected to be similar to the spectrum of a free H₂O molecule. Figure 4 confirms these expectations, because the acceptor and free molecule spectra both have the same basic structure of two peaks at approximately the same energy level. The absorption spectrum of the donor molecule shows two peaks as well as a band of higher energies, which is very different from the shape of the free molecule spectrum.

Acceptor v. donor

The spectra of the acceptor and donor molecules also behave differently as the H bond breaks. The H bond breaks when lengthening the H bond, because the greater distance weakens the electrostatic interactions between the two molecules. As shown in Figure 5, breaking the H bond causes the acceptor molecule's peak energy levels to decrease slightly. This shift with decreasing confinement of the molecules is expected, from the particle in a box analogy. In contrast to the acceptor molecule spectra, the donor molecule spectra in Figure 6 display much more drastic changes when the H bond is

broken, notably the appearance and then disappearance of a third peak (detailed discussion later). These changes in the spectra indicate changes in the unoccupied molecular orbitals of the donor molecule. Therefore following the changes in the donor molecule absorption spectra can accurately monitor changes in the H-bonding in the water dimer.

A similar situation appears when the O-H...O angle is decreased. Changing the angle can be seen as breaking the H bond, just like lengthening the H bond. This is because the oxygen lone pairs, which are more or less fixed in position by the acceptor molecule's repulsive O-H bonds, are being rotated away from the hydrogen atom. This will also decrease the electrostatic interactions, thus breaking the H bond. As a result, it is reasonable to expect similar changes in the absorption spectra from changing O-H...O angle as from lengthening the H bond. Figures 5, 7, and 8 confirm this reasoning.

Drastic changes involving a third peak can be seen in the donor molecule in Figures 7 and 8, whereas the acceptor molecule only shows slight shifts to lower energies in Figure 5.

From these observations, it can be concluded that breaking the H bond does not affect the unoccupied molecular orbitals, and thus the absorption spectra, of the acceptor molecule. This conclusion correlates with past studies of bulk water. These studies calculated theoretical absorption using systems of thirty to forty H₂O molecules (Cavalleri, 2002). In some systems, the H bond was broken at the hydrogen site of the central molecule in the distorted tetrahedron. In other systems the H bond was broken at the oxygen site of the central molecule in the distorted tetrahedron. These two geometrical configurations clearly represent the same difference that is seen between the acceptor and donor molecules of the dimer. The absorption spectra for broken bonds at

the hydrogen site were not significantly different from the absorption spectra of a system with no broken H bonds. The absorption spectra for broken bonds at the oxygen site did show significant differences (Myneni et al, 2002). Therefore breaking an H bond on the oxygen site could not explain why the absorption spectra of liquid water are different from the absorption spectra of ice. Breaking an H bond on the hydrogen site, on the other hand, might be able to provide such an explanation. The focus can now be shifted to the donor molecule, and how the donor molecule spectra change with the individual variables.

H bond length and O-H...O angle

As explained previously, lengthening the H bond distance and decreasing the H bond angle both effectively break the H bond. Figures 6, 7, and 8 confirm this, showing similar changes in the absorption spectra as the H bond lengthens and in both cases of the O-H...O angle decreasing. Figures 7 and 8 show that there seem to be little difference between the two cases of changing O-H...O angle, and so the angle measurements will only be referred to once. At first, breaking the H bond causes a third peak to appear. This peak dominates over the first two peaks (H bond length 2.43Å, O-H...O angle 111°, see Figure 6c, 7c, and 8c) before merging into the second peak (H bond length 3.43Å, O-H...O angle 81°, see Figure 6e, 7d, and 8d). In the end, there are once again two peaks (H bond length 5.43 Å, O-H...O angle 51°, see Figure 6f, 7f, and 8f), and the shape of the spectrum converges to the shape of the acceptor molecule/free molecule absorption spectra. The similarity of the spectra for the molecules at large distances and the free molecule is expected, because the acceptor molecule spectra represents a molecule which is unaffected by the presence of an H bond. As mentioned before, breaking the H bond affects the unoccupied molecular orbitals of the donor molecule. It can also be observed

that these effects are present for H bond lengths of 5 Angstroms even. The graphs shown in Figure 6 are insufficient to quantify an exact length at which the H bond breaks.

H bond strength

It is instructive to plot the H bond strength as a function of distances and angles as shown in Figure 10. The graphs are one-dimensional slices of a multi-dimensional plot that would show H bond strength as a function of all possible positions and orientations. The graphs in Figure 10 give another idea of the range of distances over which the H bond is present. Yet it still seems difficult to quantify an exact point at which the H bond is no longer present from this graph.

The intermolecular interactions which created these potential curves are repulsion, electrostatic interactions, and charge transfer. The graphs of Figure 10 provide opportunities to quantify the effects charge transfer. More calculations will follow the ones presented here to address this issue.

Dihedral angle

It can be reasoned that changing the dihedral angle in either direction will have little effect on the absorption spectra, because the rotation will not change the position of the hydrogen atom relative to the two lone pairs on the oxygen atom. This indicates that the relative positions of the oxygen lone pairs and the hydrogen atom would have to be changed in order to create changes in the H bond and the absorption spectra. This is true for both acceptor and donor molecules. As expected, changing the dihedral angle in either direction produces almost no change in the absorption spectra in Figure 9. From this, it can be reasoned that changing the dihedral angle while changing the O-H...O angle will have negligible effects on the absorption spectra of the acceptor and donor molecules.

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I would like to extend my gratitude to my mentor Professor Anders Nilsson for taking me into his group and giving me the opportunity to witness and experience for myself the world of research. I would also like to thank the entire research group, especially Philippe Wernet, Matteo Cavalleri, Klas Andersson, and Lars Näslund, for the constant help and encouragement.

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Figures

Figure 1. H_2O phase diagram

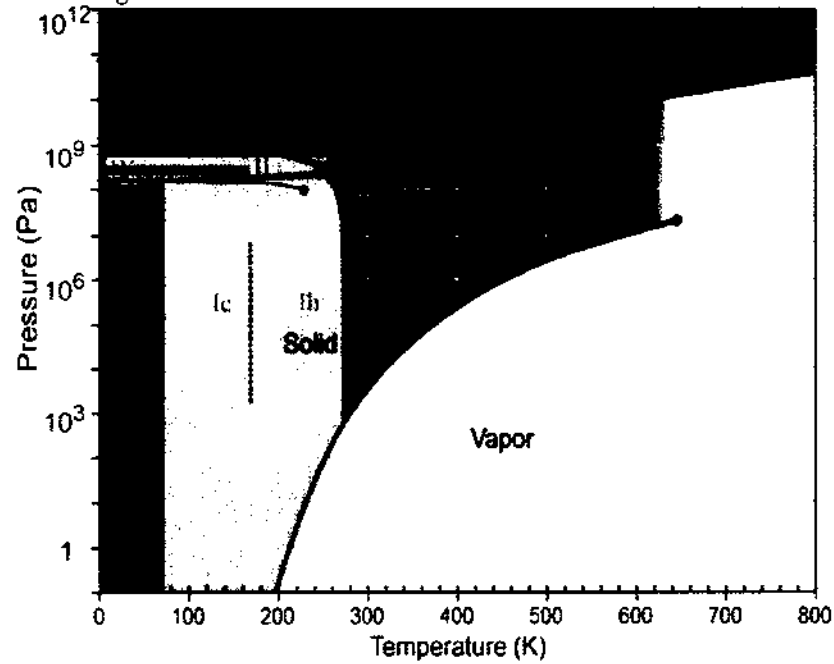


Figure 1. Phase diagram for water. Ice Ih can be formed over a wide range of temperatures and pressures, but is most commonly formed at 0°C and at atmospheric pressure (Chaplin, 2002)

Figure 2. Tetrahedral structure of ice Ih.

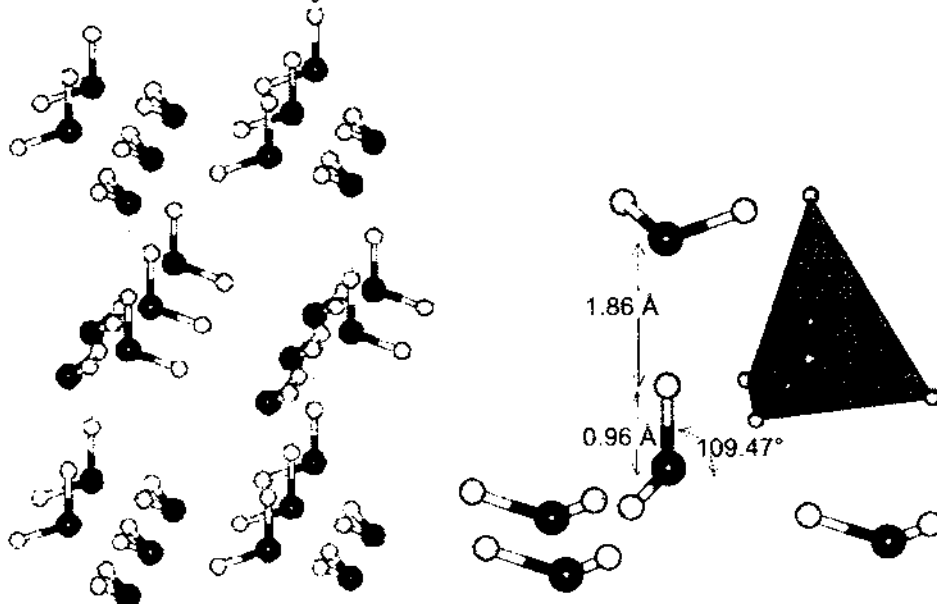


Figure 2. The tetrahedral structure formed by ice Ih (Chaplin, 2002).

Figure 3. Water dimer, hydrogen bond length, O-H...O angle, and dihedral angle

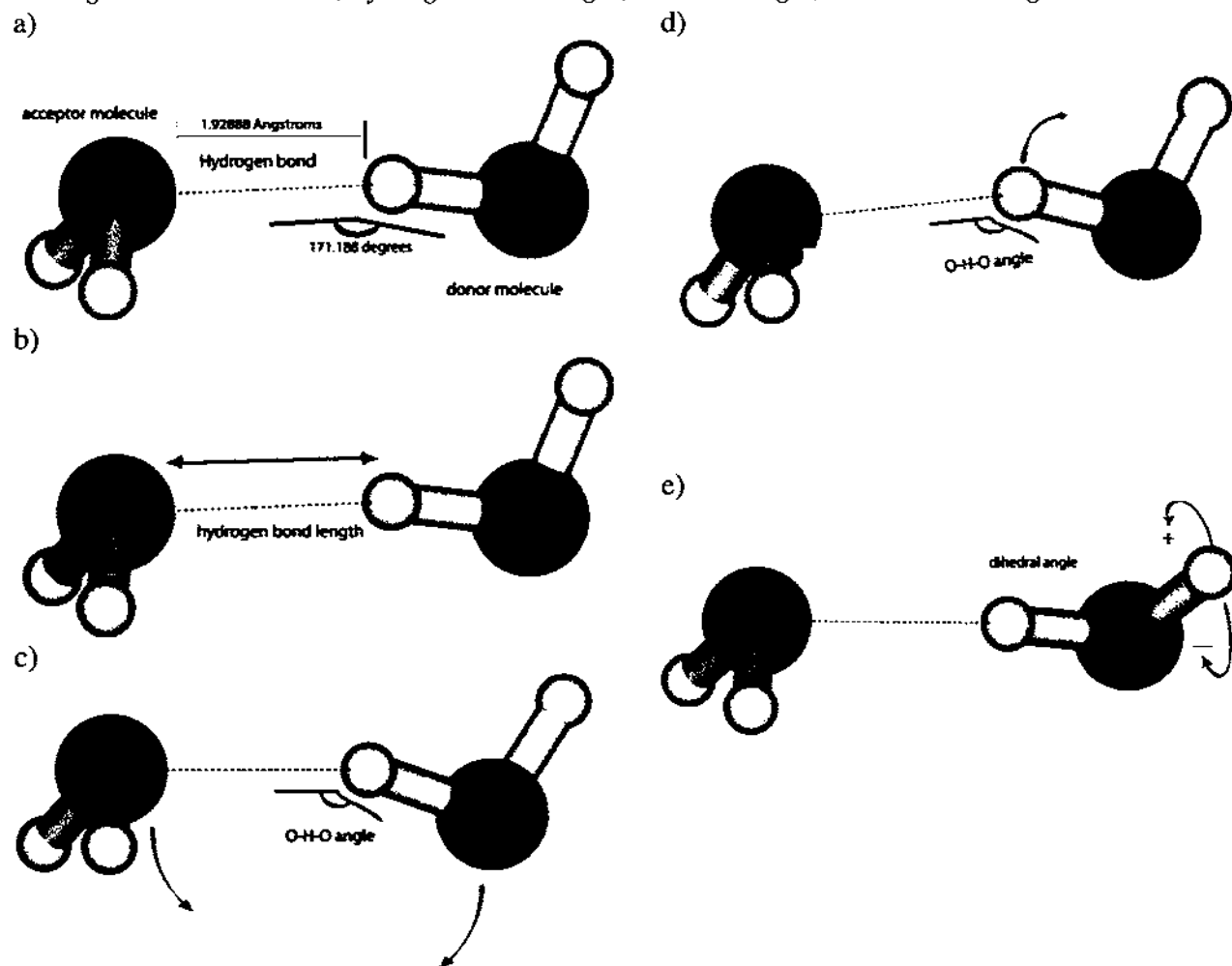
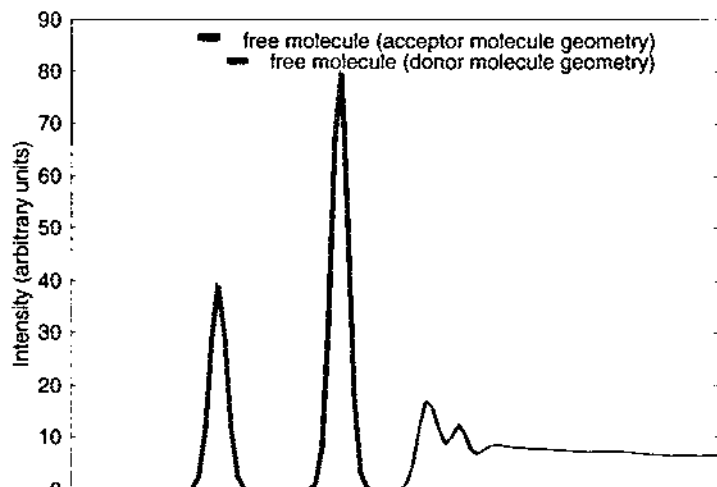


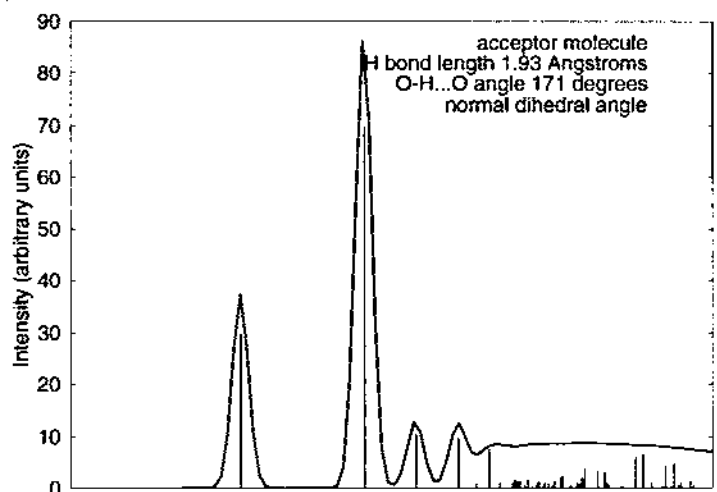
Figure 3 shows a) optimized dimer geometry, b) how the hydrogen bond length is changed, c) how the O-H...O angle is changed while the H-bond length is kept constant, d) how the O-H...O angle is changed while the O O distance is kept constant, and e) how the dihedral angle is changed. The intramolecular geometry of each individual molecule is kept constant through this whole process.

Figure 4. Comparing the x-ray absorption spectra of the free H_2O molecule and acceptor and donor molecule in the optimized water dimer.

a)



b)



c)

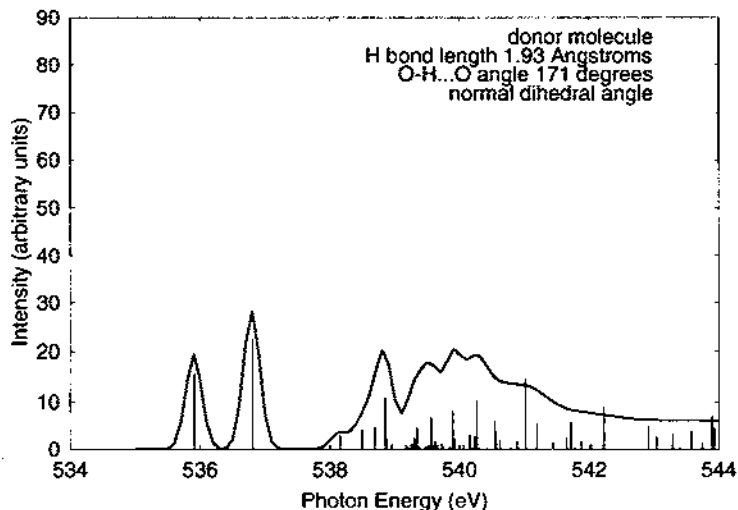


Figure 4 shows the x-ray absorption spectra of the a) free molecule with acceptor molecule geometry (same geometry as the acceptor molecule in the optimized dimer) and the free molecule with donor molecule geometry (same geometry as the donor molecule in the optimized dimer) b) the acceptor molecule in the optimized water dimer, and c) the donor molecule in the optimized water dimer.

Figure 5. X-ray absorption spectra of acceptor molecule for changing H bond length and O-H...O angles

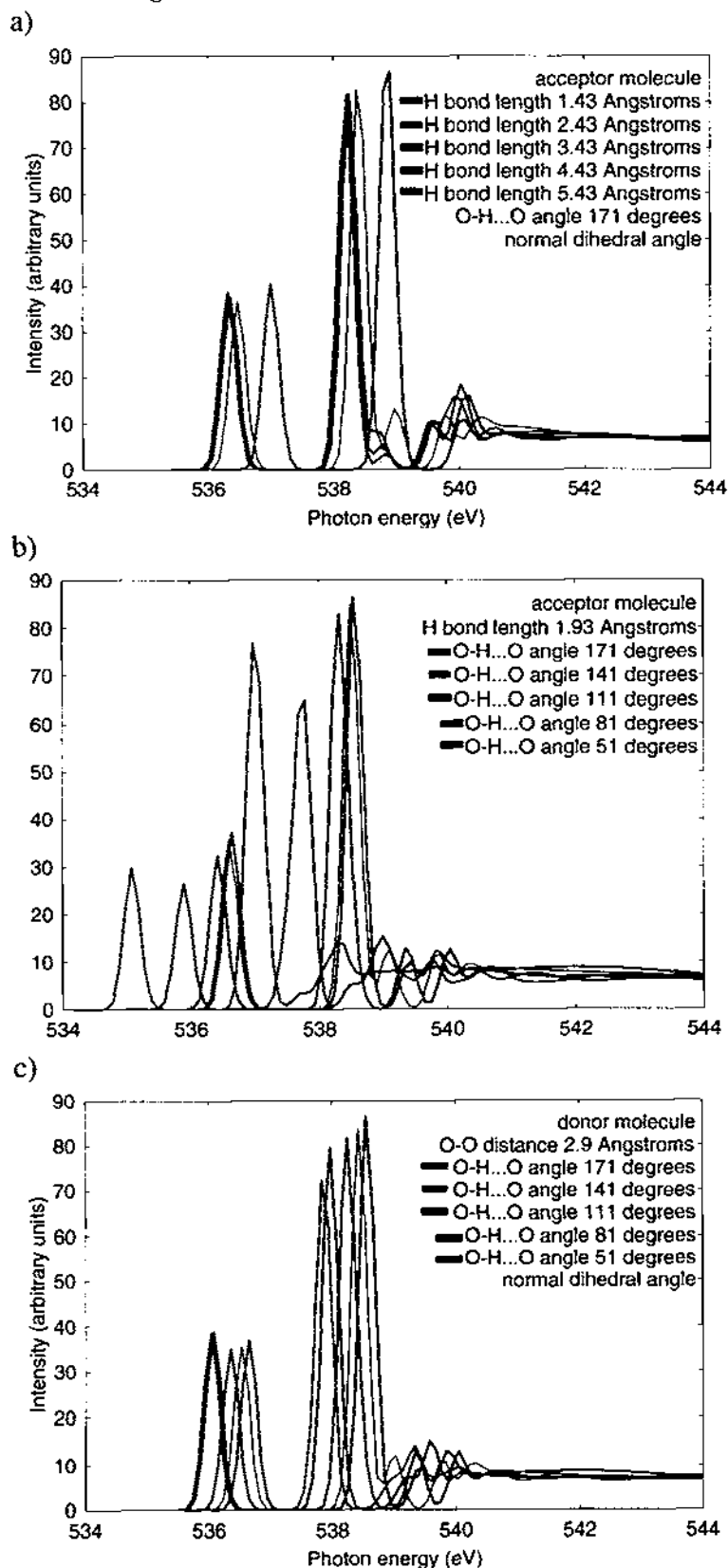
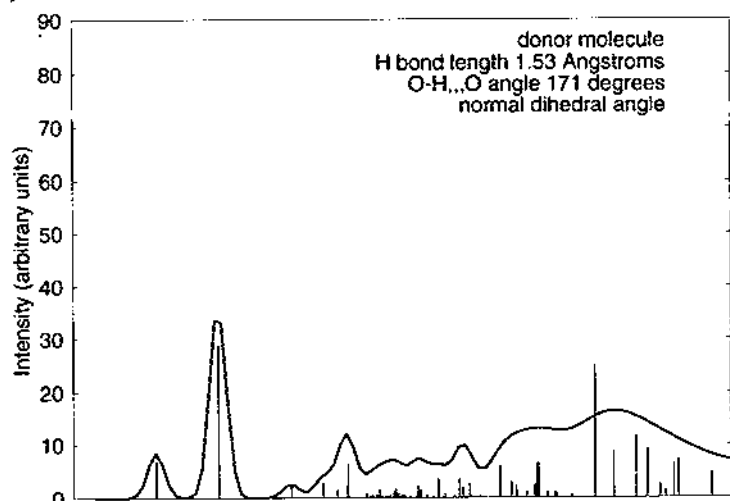


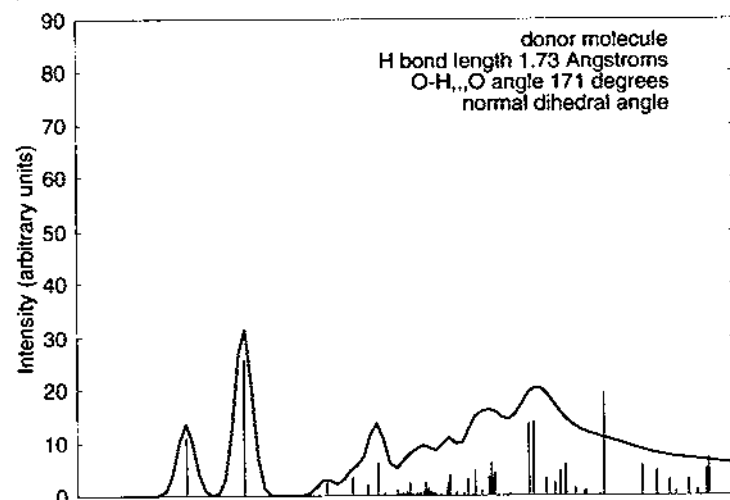
Figure 5 shows the progression of x-ray absorption spectra of the acceptor molecule as the a) H bond length varies, b) the O-H...O angle is varied with the H-bond length constant, and c) the O-H...O angle is varied with the O O distance constant. The H bond length of the optimized dimer is 1.93Å, and the O-H...O angle is 171°.

Fig. 6. X-ray absorption spectra of donor molecule for changing H bond length

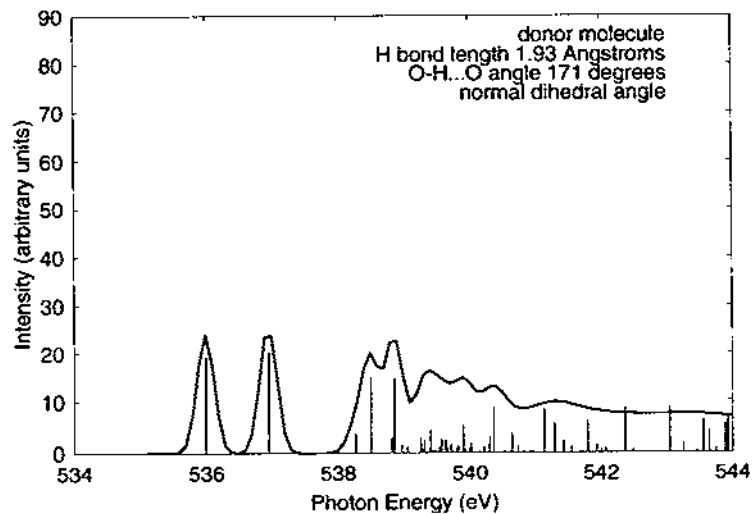
a)

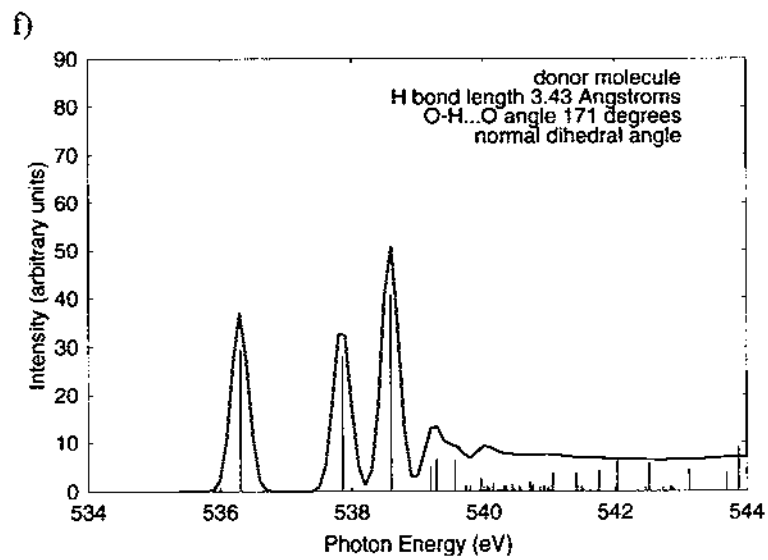
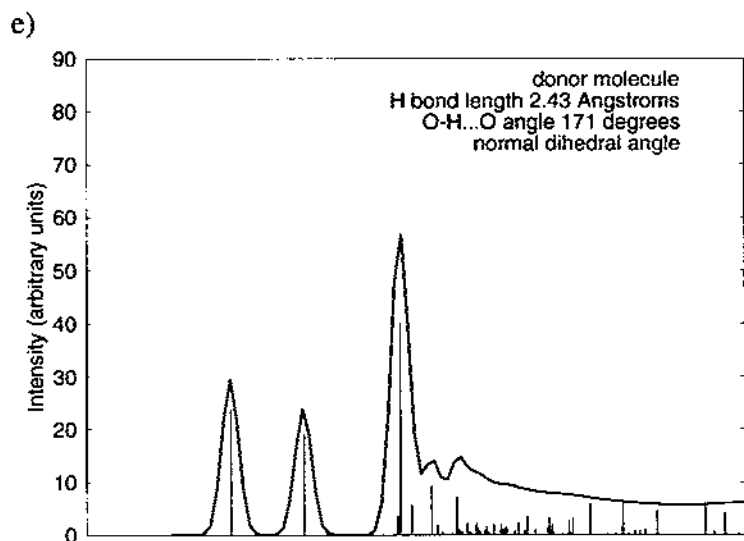
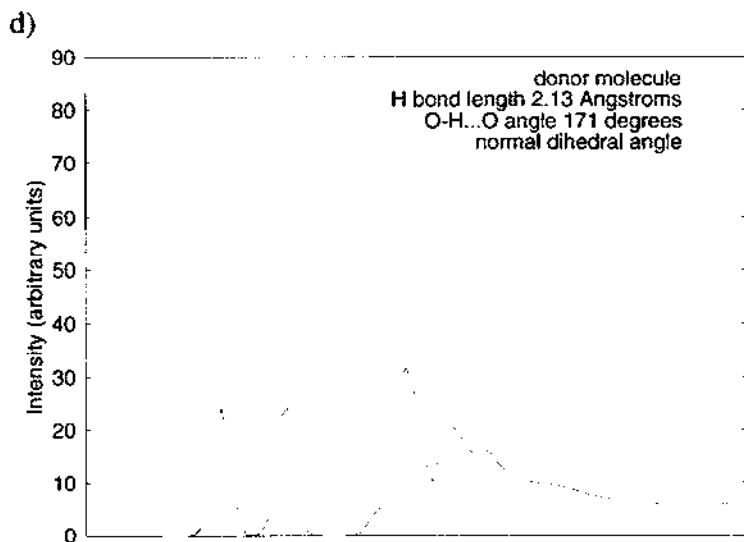


b)



c)





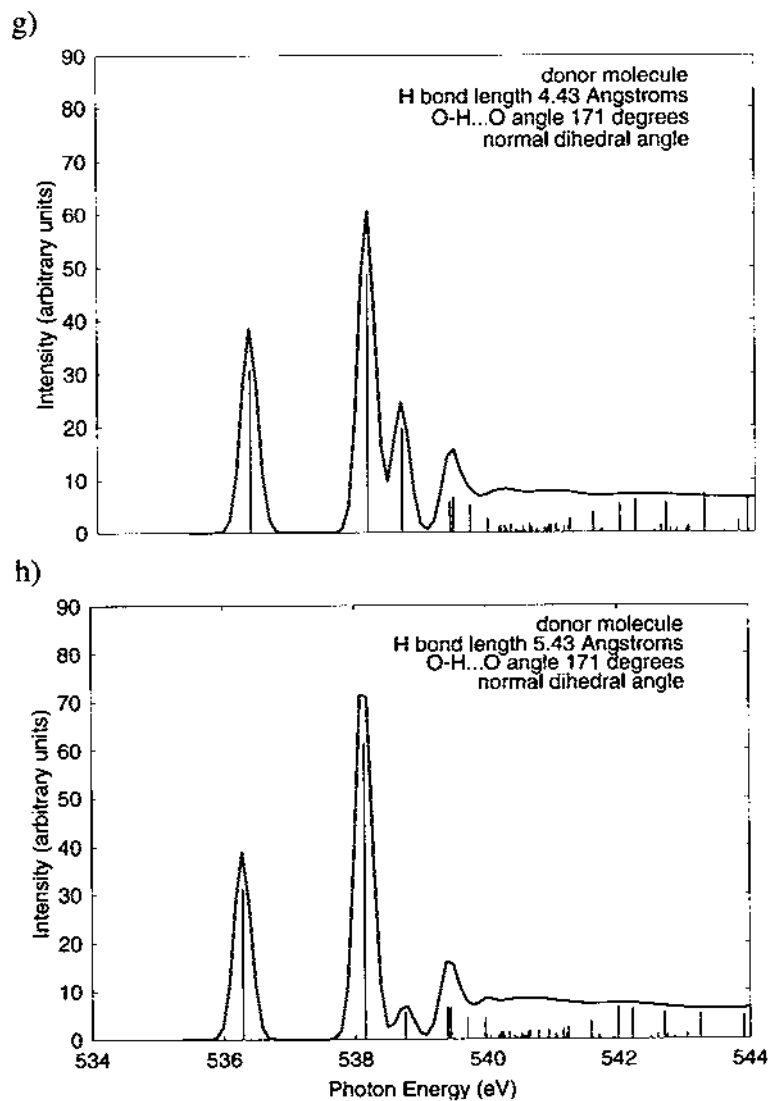
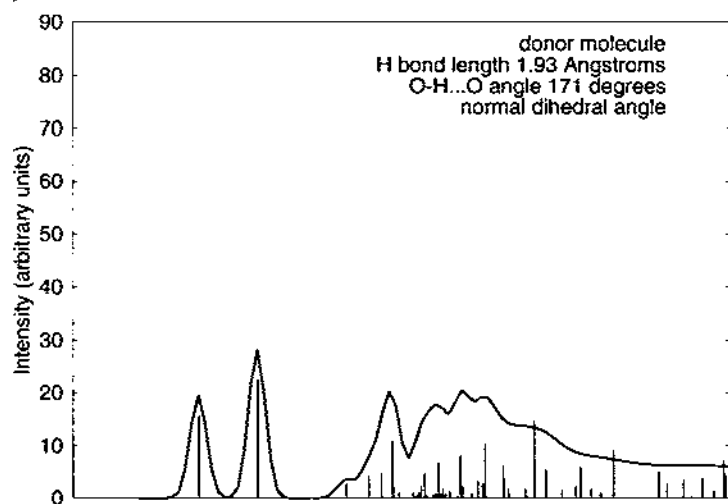


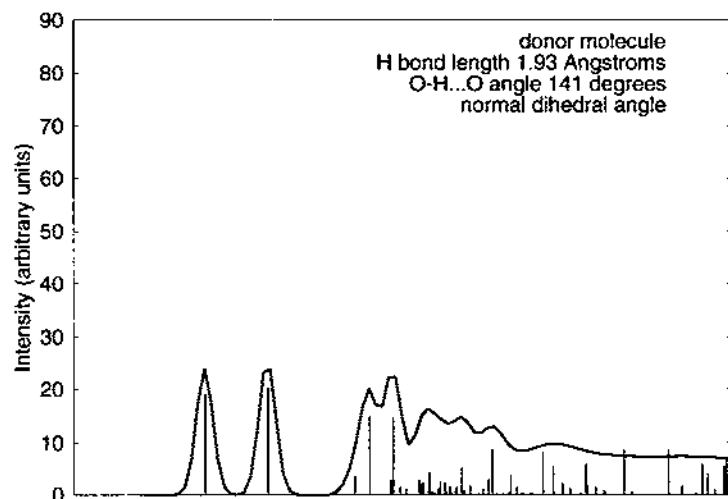
Figure 6 shows the progression of x-ray absorption spectra of the donor molecule as the H bond length changes. All other angles and distances are unchanged from the optimized geometry of the water dimer. a) Absorption spectra for hydrogen bond length 1.53Å, b) 1.73 Å, c) 1.93 Å, d) 2.13 Å, e) 2.43 Å, f) 3.43 Å, g) 4.43 Å, and h) 5.43 Å. The H bond length of the optimized dimer is 1.93Å.

Figure 7. XAS of donor molecule for changing O-H...O angle, maintaining H bond length

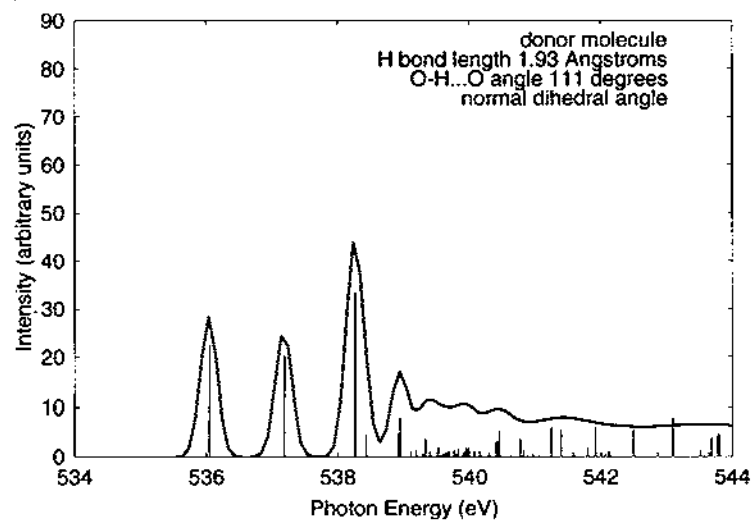
a)



b)



c)



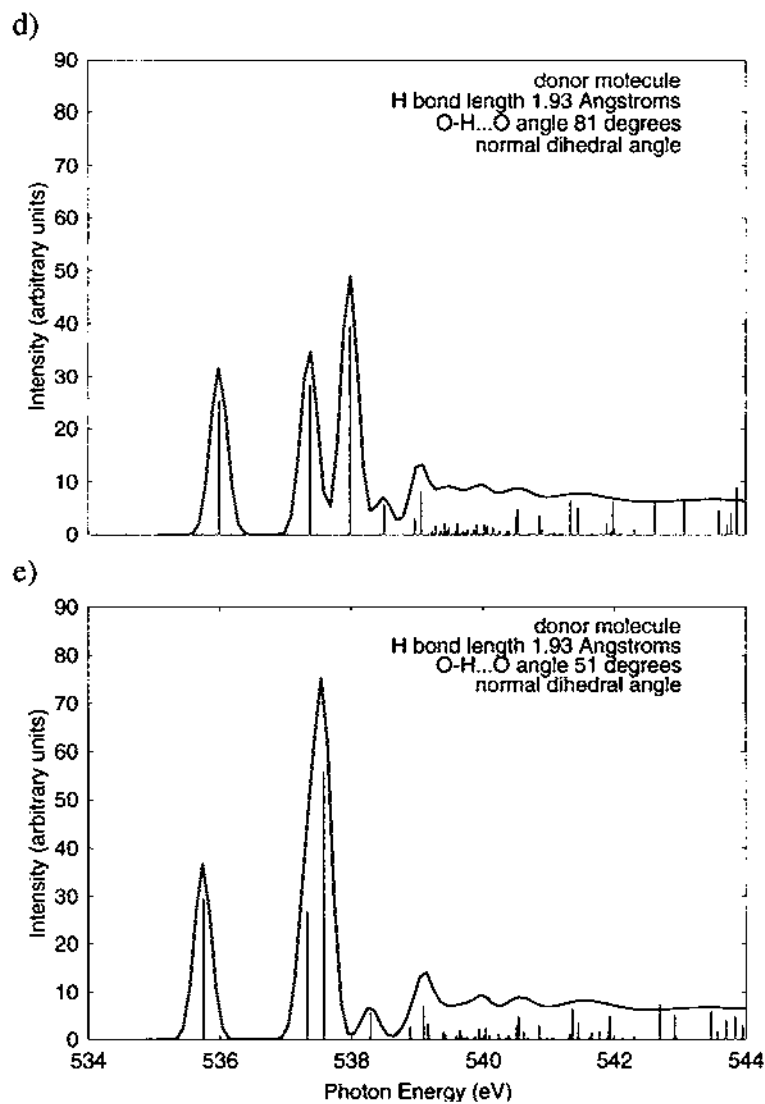
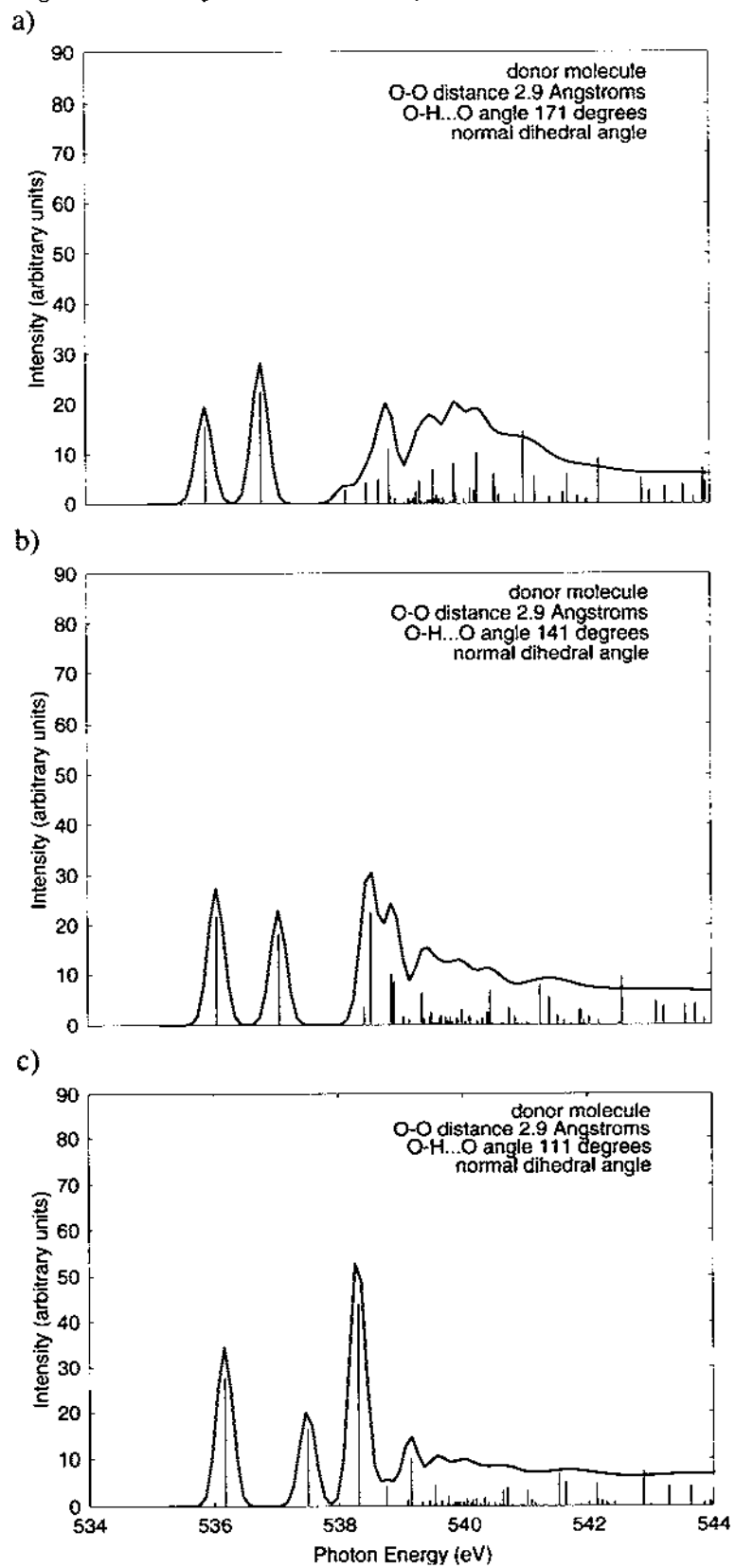


Figure 7 shows the progression of x-ray absorption spectra of the donor molecule as the O-H...O angle changes while the H-bond length is kept constant. All other angles and distances are unchanged from the optimized geometry of the water dimer. a) Absorption spectra for angle 171°, b) 141°, c) 111°, d) 81°, and e) 51°. The O-H...O angle of the optimized dimer is 171°.

Figure 8. XAS of donor molecule for changing O-H...O angle, maintaining O O distance



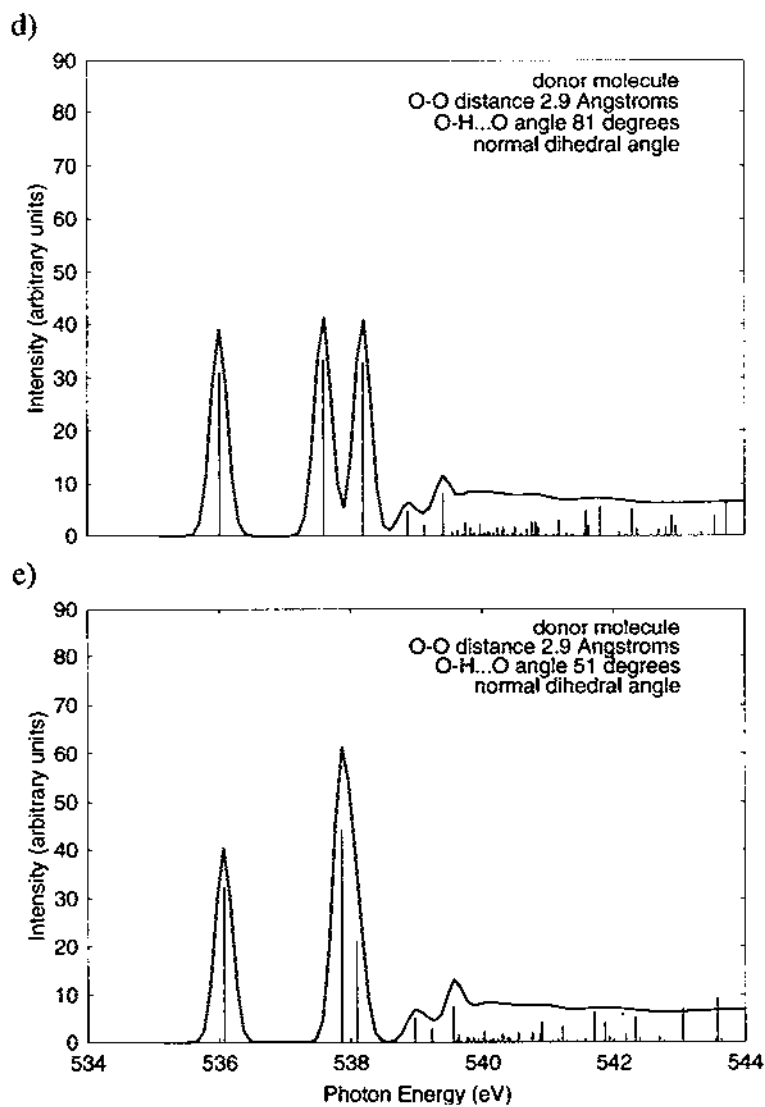


Figure 8 shows x-ray absorption spectra of the donor molecule for changing the O-H...O angle while keeping the O O distance constant. Shown are absorption spectra for a) 171°, b) 141°, c) 111°, d) 81°, and e) 51°. The O-H...O angle of the optimized dimer is 171°.

Figure 9. X-ray absorption spectra for changing dihedral angle

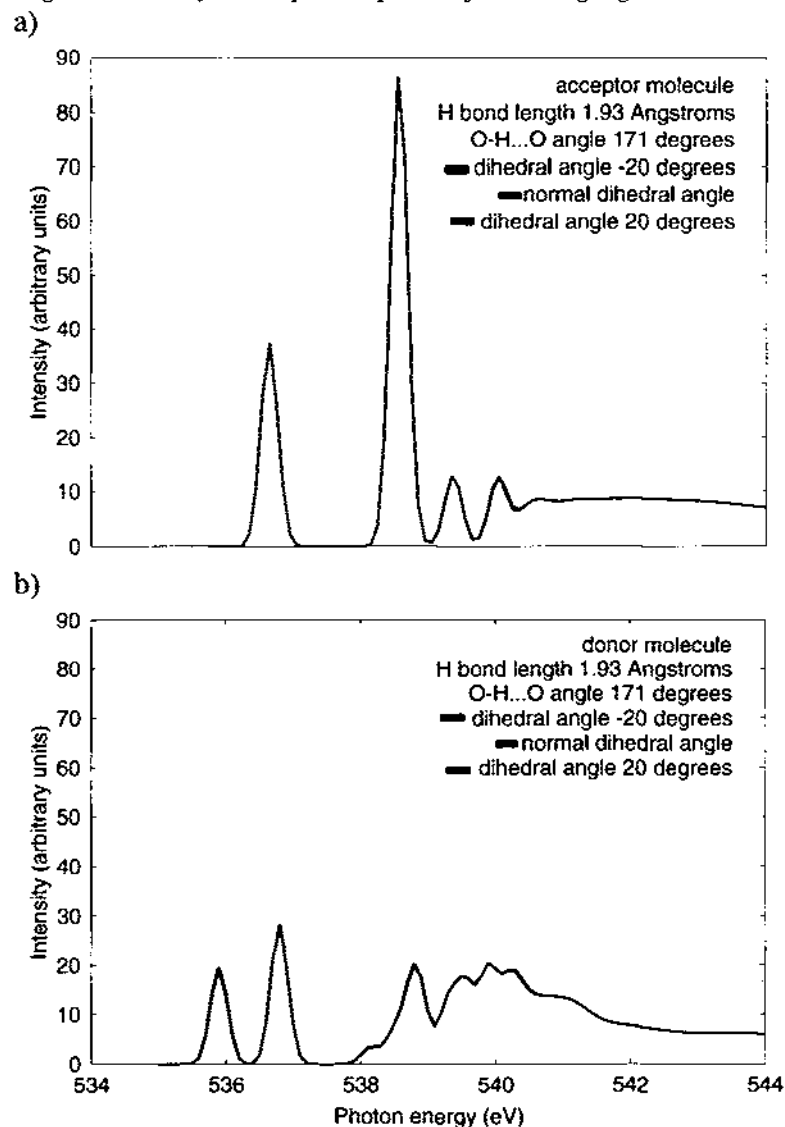


Figure 9 shows the progression of x-ray absorption spectra for the a) acceptor and b) donor molecule, as the dihedral angle (see text) is changed. The spectra obtained by rotating the planes 20° in both directions are overlaid with the spectrum for the optimized geometry. Since the spectra are extremely similar, only the blue curve is visible for the most part. Normal dihedral angle is considered as the dihedral angle of the optimized dimer.

Figure 10. Ground state and final excited state energies

a) Ground state energies of individual water molecules:

H₂O molecule 1 (same geometry as acceptor molecule in water dimer): -2080.920631 eV

H₂O molecule 2 (same geometry as donor molecule in water dimer): -2080.8727380 eV

H bond Length (Angstroms)	Ground State Energy (eV)	H bond Strength (eV)
1.43	-4161.733411	0.059948344
1.53	-4161.890934	-0.097574963
1.63	-4161.982481	-0.189122337
1.73	-4162.031456	-0.238096811
1.83	-4162.053813	-0.260454107
1.93	-4162.057901	-0.264541507
2.03	-4162.050642	-0.25728346
2.13	-4162.037296	-0.243936712
2.23	-4162.021841	-0.228481867
2.33	-4162.006525	-0.213165933
2.43	-4161.992066	-0.198706692
2.53	-4161.979031	-0.185671626
2.63	-4161.966232	-0.172872914
2.73	-4161.953653	-0.16029375
2.83	-4161.941575	-0.14821568
2.93	-4161.930625	-0.13726647
3.03	-4161.92133	-0.127970854
3.13	-4161.913723	-0.120363952
3.23	-4161.908373	-0.115014388
3.33	-4161.903851	-0.11049222
3.43	-4161.899732	-0.106373015
3.53	-4161.89536	-0.102001363
3.73	-4161.886864	-0.093504984
3.93	-4161.879057	-0.08569774
4.13	-4161.873457	-0.080098248
4.33	-4161.867873	-0.074513802
4.43	-4161.86751	-0.074150878
4.53	-4161.866571	-0.073211882
4.73	-4161.864437	-0.07107751
4.93	-4161.861964	-0.068604623
5.13	-4161.859091	-0.065731503
5.33	-4161.857708	-0.064348626
5.43	-4161.856707	-0.063347818
5.53	-4161.855772	-0.062413459

c)

H bond strength for changing O-H...O angle (maintaining H bond length) in the water dimer

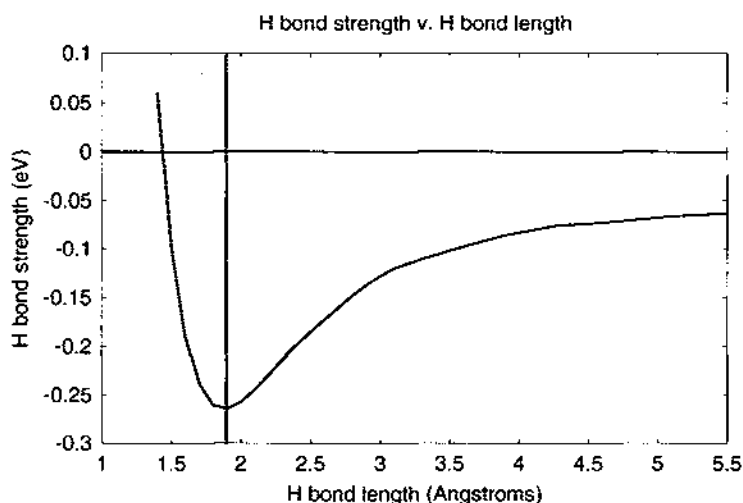
H bond Length (Angstroms)	Ground State Energy (eV)	H bond Strength(eV)
179	-4162.054308	-0.26094853
175	-4162.056729	-0.263369772
171	-4162.057901	-0.264541507
167	-4162.057766	-0.264407283
163	-4162.055584	-0.26222525
159	-4162.05142	-0.258060618
155	-4162.045539	-0.252180305
151	-4162.038403	-0.245044289
147	-4162.029976	-0.236617488
143	-4162.01986	-0.226500917
139	-4162.007428	-0.214069445
135	-4161.992098	-0.19873927
131	-4161.97363	-0.180270678
127	-4161.951102	-0.157742777
123	-4161.923619	-0.130260277
119	-4161.891015	-0.097656154
115	-4161.852413	-0.059054268
111	-4161.806199	-0.012839657
107	-4161.751459	0.041899568
103	-4161.686065	0.10729412
99	-4161.605033	0.188326384
95	-4161.503693	0.289665841
91	-4161.377051	0.416308301
86	-4161.16881	0.624548804
81	-4160.881648	0.911710609
76	-4160.487583	1.305776249
71	-4159.952395	1.840963665
66	-4159.237143	2.556215978
61	-4158.284539	3.508819572
56	-4157.01489	4.778469118
51	-4155.36807	6.425289454

d)

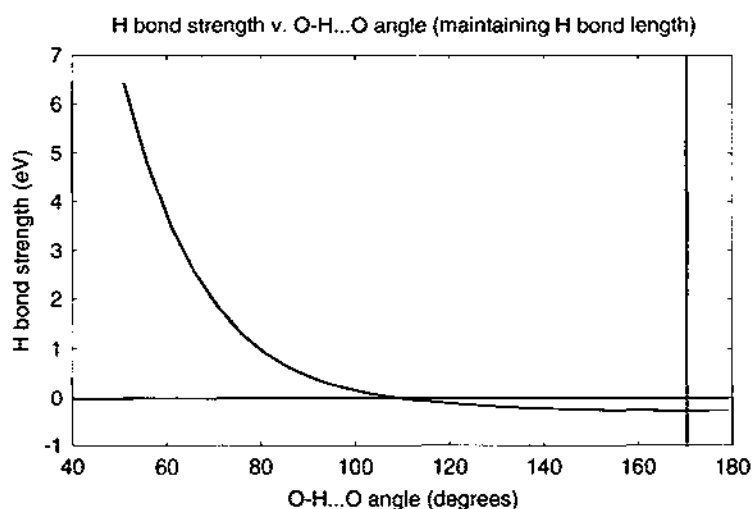
H bond strength for changing O-H...O angle (maintaining O O distance) in the water dimer

H bond Length (Angstroms)	Ground State Energy (eV)	H bond Strength (eV)
171	-4162.057939	-0.264580476
166	-4162.056895	-0.263536258
161	-4162.052235	-0.258876296
156	-4162.044069	-0.250709622
151	-4162.032558	-0.239199148
146	-4162.018578	-0.225219079
141	-4162.002955	-0.209595754
136	-4161.985887	-0.192527803
131	-4161.96789	-0.174530685
126	-4161.949425	-0.156065911
121	-4161.930687	-0.1373276
116	-4161.911911	-0.118552124
111	-4161.89397	-0.100610817
106	-4161.877091	-0.083732346
101	-4161.860802	-0.067443349
96	-4161.844208	-0.050849054
91	-4161.826916	-0.033557331
90	-4161.823386	-0.030027089
89	-4161.819763	-0.02640424
88	-4161.815833	-0.022474319
87	-4161.810755	-0.017395899
86	-4161.802578	-0.009219464
85	-4161.773307	0.020051521
84	-4161.717263	0.076096151
83	-4161.711176	0.082183315
82	-4161.709238	0.084120966
81	-4161.707088	0.086270748
76	-4161.697683	0.095675866
71	-4161.68969	0.103668664
66	-4161.684204	0.109154825
61	-4161.680827	0.11253176

e)



f)



g)

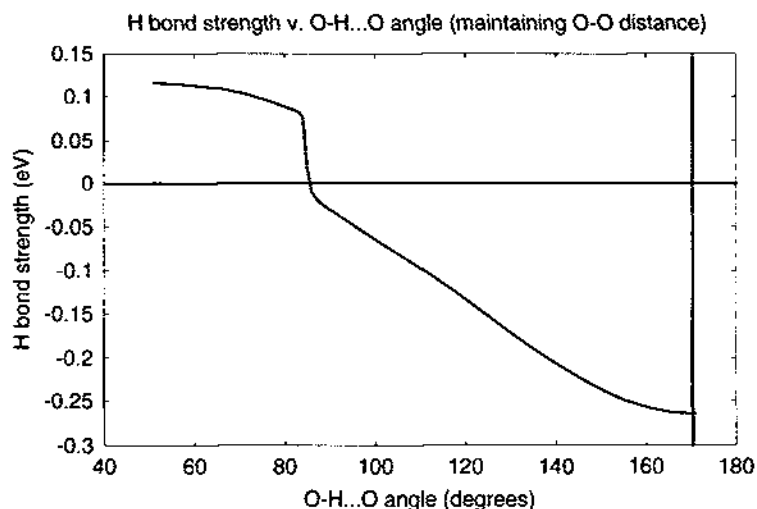


Figure 10 shows calculated energy data for a) two individual H_2O molecules with the same geometry as their counterparts in the optimized dimer, b) calculated dimer ground state energy and hydrogen bond strength for given H-bond lengths, c) calculated dimer ground state energy and hydrogen bond strength for given O-H...O angles (maintaining constant H bond length), d) calculated dimer ground state energy and hydrogen bond strength for given O-H...O angles (maintaining constant O O distance), e) graph of H bond strength as a function of H bond length, f) O-H...O angle maintaining constant hydrogen bond length, and g) O-H...O angle maintaining a constant O O distance. The tables are highlighted blue where the energies of the optimized dimer are shown. The graphs have a vertical line indicating the optimized geometry.