

# WATER STRUCTURE AND BEHAVIOR

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Search



Text



## Molecular Vibration and Absorption

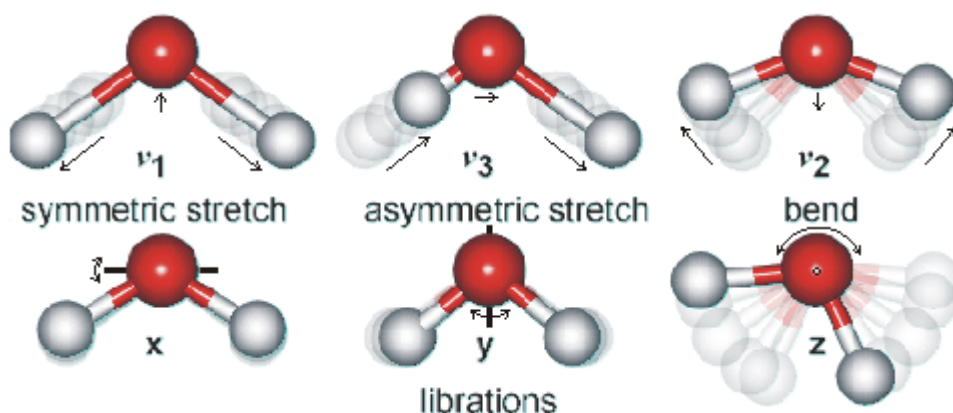
Water is the main absorber of the sunlight. The 13 million million tons of water in the atmosphere ( $\sim 0.33\%$  by weight) is responsible for about 70% of all atmospheric absorption of radiation, mainly in the infrared region where water shows strong absorption. It contributes significantly to the greenhouse effect ensuring a habitable planet, but operates a negative feedback effect, due to cloud formation, to attenuate global warming.

Water vapor spectroscopy has been recently reviewed [348]. The water molecule may vibrate in a number of ways. In the gas state, the vibrations [607] involve combinations of symmetric stretch ( $\nu_1$ ), asymmetric stretch ( $\nu_3$ ) and bending ( $\nu_2$ ) of the covalent bonds with absorption intensity ( $\text{H}_2^{16}\text{O}$ )  $\nu_1; \nu_2; \nu_3 = 0.07; 1.47; 1.00$  [8]. The stretch vibrations of  $\text{HD}^{16}\text{O}$  refer to the single bond vibrations, not the combined movements of both bonds.

Main vibrations of water isotopologues

Gas	$\nu_1, \text{cm}^{-1}$	$\nu_2, \text{cm}^{-1}$	$\nu_3, \text{cm}^{-1}$
$\text{H}_2^{16}\text{O}$	3657.05	1594.75	3755.93
$\text{H}_2^{17}\text{O}$	3653.15	1591.32	3748.32
$\text{H}_2^{18}\text{O}$	3649.69	1588.26	3741.57
$\text{HD}^{16}\text{O}$	2723.68	1403.48	3707.47
$\text{D}_2^{16}\text{O}$	2669.40	1178.38	2787.92
$\text{T}_2^{16}\text{O}$	2233.9	995.37	2366.61

Shown opposite are the main vibrations occurring in water. The movements are animated using the cursor. The dipole moments change in the direction of the movement of the oxygen atoms as shown by the arrows.



The main stretching band in liquid water is shifted to a lower frequency ( $\nu_3$ ,  $3490 \text{ cm}^{-1}$  and  $\nu_1$ ,  $3280 \text{ cm}^{-1}$  [8]) and the bending frequency increased ( $\nu_2$ ,  $1644 \text{ cm}^{-1}$  [942]) by hydrogen bonding.

Main vibrations of liquid ordinary and heavy water

Vibration [942]	liquid H <sub>2</sub> O (25°C)		liquid D <sub>2</sub> O (25°C)	
	$\nu$ , cm <sup>-1</sup>	$E_0$ , M <sup>-1</sup> cm <sup>-1</sup>	$\nu$ , cm <sup>-1</sup>	$E_0$ , M <sup>-1</sup> cm <sup>-1</sup>
$\nu_2$	1643.5	21.8	1209.4	17.4
$\nu_2$ + libration	2127.5	3.50	1555.0	1.91
$\nu_1 + \nu_3 + \nu_2$ (overtone)	3404.0	99.9	2504.0	71.5

Variations in the environment around each liquid water molecule gives rise to considerable line broadening with vibration shifts in a hydrogen-bond-donating water molecule being greater than in a hydrogen-bond accepting molecule but both acting in the same direction [679], and accumulating with the number of hydrogen bonds. The strength of the hydrogen bonding depends on the [cooperative/anticooperative nature of the surrounding hydrogen bonds](#) with strongest hydrogen bonds giving the lowest vibrational frequencies [852]. Stretching frequency increases about 360 (at 3.1 Å) -1000 (at 2.6 Å) cm<sup>-1</sup>Å<sup>-1</sup> with increasing O····O distance and about 9 cm<sup>-1</sup> degree<sup>-1</sup> with increasing O-H····O bend [446]. The absorption intensity of these bands is  $\nu_1; \nu_2; \nu_3 = 0.87; 0.33; 1.00$  [8]. In

supercooled water, the spectra is shifted to lower frequency with a 70 cm<sup>-1</sup> shift of the stretch frequency and 30% increase in its intensity between 298 K and 238 K [1065]. In ice, these bands are shifted further ( $\nu_1$ , 3085 cm<sup>-1</sup>,  $\nu_2$ , 1650 cm<sup>-1</sup>,  $\nu_3$ , 3220 cm<sup>-1</sup>). In liquid water the molecular stretch vibrations shift to higher frequency, on raising the temperature (as hydrogen bonding weakens, the covalent O-H bonds strengthen causing them to vibrate at higher frequencies) whereas the intramolecular vibrations shift to lower frequencies and the molecular bend vibration peak both shifts to lower frequencies and becomes narrower [696]. Raising the temperature also lowers the intensity of the stretching bands. This divergent behavior of bending and stretching vibrations allows their contributions to combination bands to be discerned. Thus, combinations of stretching vibrations shift to higher frequency with temperature with this trend reduced when bending vibrations are also combined. As examples, the first overtone combination of symmetric and asymmetric stretching shows a shift from strongly hydrogen-bonded structures (6707 cm<sup>-1</sup>) to weakly hydrogen bonded structures (7082 cm<sup>-1</sup>) with increasing temperature [237], and the combination band at about 5200 cm<sup>-1</sup> shifts to slightly higher wavenumbers with reduced hydrogen bond strength [282]. The second overtone of the stretching band gives rise to a significant peak in the near-infrared spectrum ( $\lambda$  970 nm). Recent work shows that the intensity of all overtone bands tend to increase linearly with increasing temperature in the range 2°C - 85°C without isobestic points (in contrast to earlier reports [530]), so ruling out a simple two-phase model for water [526]. However IR evanescent wave spectroscopy does show isobestic points in the O-H stretch region [699]. These apparently confused conclusions may be more supportive of progressively changing two-phase models such as [described here](#). Increasing the pressure on water decreases the O····O distances ([graphed elsewhere](#)) so increasing the covalent O-H

distances and lowering their stretch frequency [804]. Raised pressure also causes a reduction in long, weak or broken bonds and an increase in bent and short, strong hydrogen bonds [804]. ▲

In liquid water and ice the **infrared and Raman spectra** are far more complex than the vapor due to vibrational overtones and combinations with librations (restricted rotations; *i.e.* rocking motions). These librations are due to the restrictions imposed by **hydrogen bonding** (minor  $L_1$  band  $395.5\text{ cm}^{-1}$ ; major  $L_2$  band  $686.3\text{ cm}^{-1}$ ; both at  $0^\circ\text{C}$ , the absorbance of  $L_1$  increasing with increasing temperature whereas  $L_2$  absorbance decreases but broadens with reduced wavenumber with increasing temperature [177]). The librations depend on the **moments of inertia** such that the almost doubling of the moments of inertia of  $\text{D}_2\text{O}$ , relative to  $\text{H}_2\text{O}$ , reduces the frequencies by about a factor of  $\sqrt{2}$ . Cluster vibrations such as translational vibrations involve combinations of hydrogen bond  $\text{O-H}\cdots\text{O}$  stretching and bending at around  $200\text{ cm}^{-1}$  (6 THz) [240] (S or connectivity band,  $183.4\text{ cm}^{-1}$  (5.5 THz); at  $0^\circ\text{C}$ , the hydrogen bond stretch absorbance increasing with decreasing temperature [819]<sup>a</sup>;  $229\text{ cm}^{-1}$  (6.9 THz) in ice Ih). These involve movements along linear or near-linear hydrogen bonds and show relatively small differences between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ , due to their slightly different masses [1004]. Bending vibrations of the hydrogen bonds also occur, due to out of alignment translations relative to the hydrogen bonds (B band  $\sim 40 - 60\text{ cm}^{-1}$  (1.2-1.8 THz); at  $0^\circ\text{C}$ , the absorbance increasing with temperature [608]) [1004]. Also in liquid water there is a small but significant combination band (IR and Raman) of the bending ( $\nu_2$ ) and libration modes at  $2125\text{ cm}^{-1}$  ( $2270\text{ cm}^{-1}$  in ice Ih; the 'association band').<sup>b</sup>

A contribution to the Raman scattering of water at  $50\text{ cm}^{-1}$  (1.5 THz) has been attributed to the low-frequency vibrations of oxygen-oxygen bonds at the vertices of pentagonal dodecahedral structures [165] or simply  $\text{O}\cdots\text{O}\cdots\text{O}$  bending motions [901]. Such low-frequency features (centered around  $60\text{ cm}^{-1}$ , 1.8 THz) are also observed in the spectra of dense non-associated liquids, such as the noble gasses, and may be attributed to non-bonded 'cage effects' where translations are frustrated [448]. This same effect, however, may also operate within hydrogen bonded 'cage effects' consistent with the  $60\text{ cm}^{-1}$  absorption band [900]. Further confirmation of the hydrogen-bonding source for this absorption comes from the use of an intense source of far infrared radiation showing temperature dependent peaks at a number of wavelengths in the  $40\text{-}90\text{ cm}^{-1}$  (1.2-2.7 THz) range [656].

The spectra for isotopic variants of water (*e.g.* HDO,  $\text{D}_2\text{O}$  and  $\text{H}_2^{18}\text{O}$ ) are all different; in particular the H-O and D-O stretching vibrations are not connected in HDO but the related vibrations in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  involve both hydrogen ato

Assignment of the IR vibrational absorption spectrum of liquid water<sup>\*</sup>

Wavelength	cm <sup>-1</sup>	Assignment	Wavelength <sup>**</sup>	cm <sup>-1</sup>	Assignment
0.2 mm	50	intermolecular bend	1470 nm	6800	$a\nu_1 + b\nu_3; a+b=2$
55 $\mu\text{m}$	183.4	intermolecular stretch	1200 nm	8330	$a\nu_1 + \nu_2 + b\nu_3; a+b=2$
25 $\mu\text{m}$	395.5	L <sub>1</sub> , librations	970 nm	10310	$a\nu_1 + b\nu_3; a+b=3$
15 $\mu\text{m}$	686.3	L <sub>2</sub> , librations	836 nm	11960	$a\nu_1 + \nu_2 + b\nu_3; a+b=3$
6.08 $\mu\text{m}$	1645	$\nu_2$ , bend	739 nm	13530	$a\nu_1 + b\nu_3; a+b=4$
4.65 $\mu\text{m}$	2150	$\nu_2 + L_2^a$	660 nm	15150	$a\nu_1 + \nu_2 + b\nu_3; a+b=4$
3.05 $\mu\text{m}$	3277	$\nu_1$ , symmetric stretch	606 nm	16500	$a\nu_1 + b\nu_3; a+b=5$ [526]
2.87 $\mu\text{m}$	3490	$\nu_3$ , asymmetric stretch	514 nm	19460	$a\nu_1 + b\nu_3; a+b=6$ [526]
1900 nm	5260	$a\nu_1 + \nu_2 + b\nu_3; a+b=1$	Note that a and b are integers, $\geq 0$ ms.		

\* Raman peaks are given in [805].

\*\*Wavelength (nm) =  $10^7/\text{wavenumber}(\text{cm}^{-1})$  (nm  $\sim$ 3.3 attosecond)

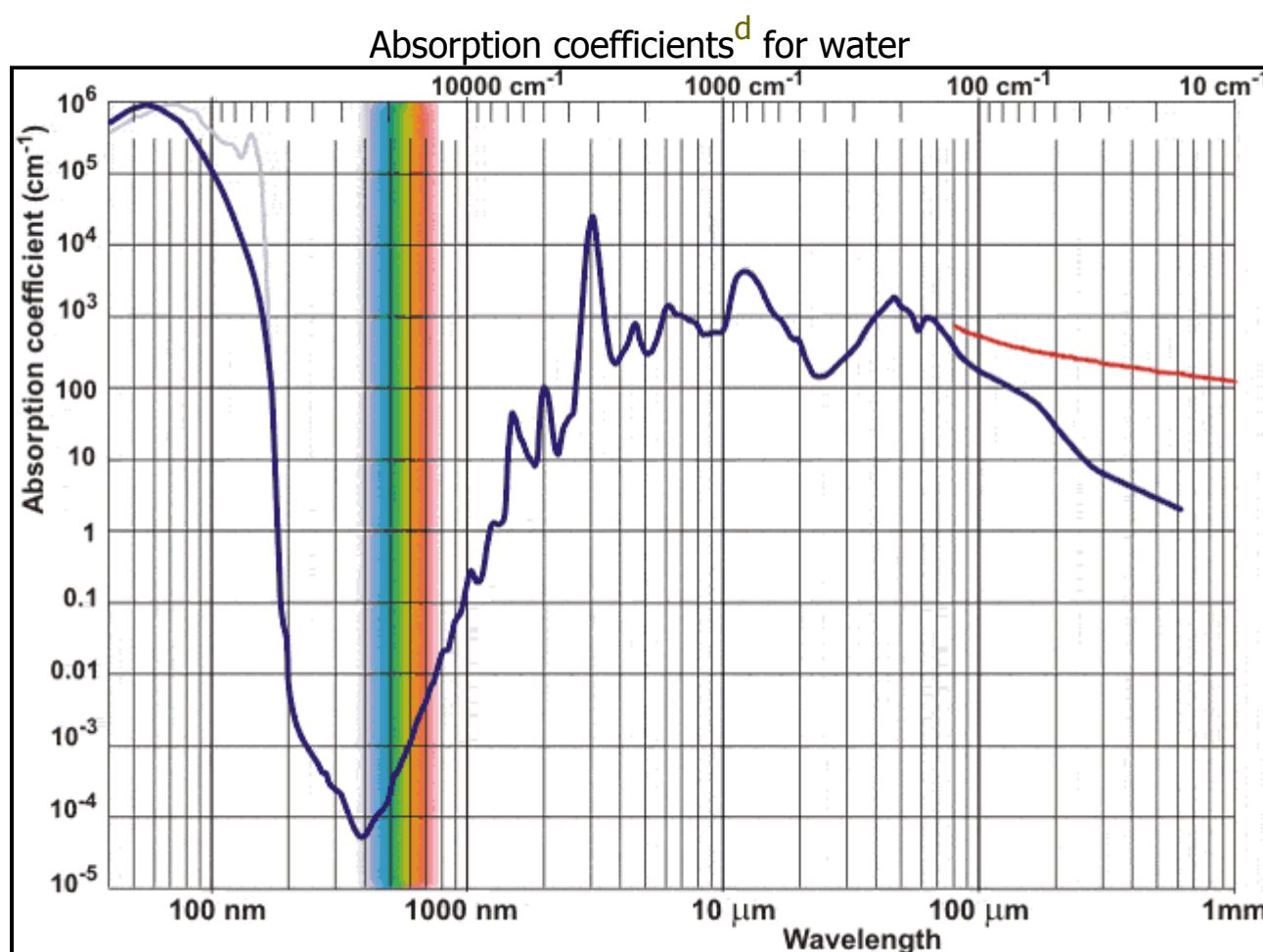
The near-infrared (NIR) bands (at about  $\lambda$  970-1940 nm) are suited to rapid non-destructive water determination [479], all shifting a few nm to longer wavelength (lower frequency) with strengthening hydrogen bonding due to shifts from high density water (*i.e.* increasing CS) to low density water (*i.e.* increasing ES) [489]. A shoulder at about  $3250 \text{ cm}^{-1}$  on the side of the only strongly active Raman peak, and recently described in the IR spectrum at  $3220 \text{ cm}^{-1}$  [699], (symmetric O-H stretch,  $\nu_1$ ) of liquid water has been assigned to the collective in-phase symmetric O-H vibrations of strongly tetrahedrally-bonded water patches. The ratio of this to the remaining peak at about  $3400 \text{ cm}^{-1}$  has been used to determine the fraction of such water but such comparisons, although commonly used, should be treated with caution, as their absorbances are unlikely to be identical and other possible vibrations, such as the first bend ( $\nu_2$ ) overtone, will interfere.

This remaining peak has been analyzed in many ways (*e.g.* as zero, single, double and triple coordinated hydrogen-bonded water) but most convincingly in terms of three-coordinate (double acceptor single donor,  $3400 \text{ cm}^{-1}$ ; single acceptor double donor,  $3535$

$\text{cm}^{-1}$ ) and two-coordinate (single acceptor single donor,  $3630 \text{ cm}^{-1}$ ) hydrogen-bonded water molecules [699]. There is clearly much structural information hidden in the vibrational spectra of water, if only it can be unambiguously interpreted (see [methods page](#)). Some success has recently been made using femtosecond mid-infrared nonlinear spectroscopy [189, 190] and the theoretical Raman spectra of water clusters [483]. ▲

Anions may be classified as [kosmotropes](#) or [chaotropes](#) according to how the effect the water's stretch vibrations; ionic kosmotropes (*e.g.*  $\text{F}^-$ ) causing broadening and movement to lower wavenumbers whereas chaotropes (*e.g.*  $\text{I}^-$ ) causing narrowing and movement to higher wavenumbers [758]. Primarily this seems due to water's ability to hydrogen bond to the anions.

The vibrational spectra of  $\text{H}_3\text{O}_2^-$  and  $\text{H}_5\text{O}_2^+$  are described on [another page](#).



## The spectrum of liquid water

Water is almost perfectly transparent to 'visible' light, a property which is made good use of by photosynthesis and allowing production of both biomass and oxygen. Water is very slightly blue in color [131]<sup>c</sup> as overtone and combination vibrational absorption bands (albeit far less intense, see above [130]) extend through the red part of the visible spectrum with a small peak at 739 nm and shoulder at 836 nm, both varying somewhat

with temperature [268] plus a smaller fourth overtone of the  $\nu_1:\nu_3$  stretch at 606 nm, and very small fifth overtone (at 514 nm) and combined overtone (at 660 nm) bands. This absorption spectrum of water (red light absorbs 100 times more than blue light), together with the five-times greater scattering of blue light over red light, contributes to the blue color of lake, river and ocean waters. Colloidal silica may contribute to the outstanding blue color of certain, often hydrothermal, pools and lakes [372]. Ice is also blue [159] for similar reasons but liquid D<sub>2</sub>O does not absorb in the red region (as the absorption band is shifted into the infrared) and is blue solely because of the light scattering effect [159]. [▲](#)

The first peak in the far UV of gaseous water (166.5 nm [902], shown light blue in the [spectrum above](#)) is due to excitation from the occupied  $p_z^2$ -type molecular  $1b_1$  orbital (interactive orbitals are available (COW only [[Plug-in, ActiveX](#)])). Absorption of UV close-by ( $\sim 125$  nm), excites the  $3a_1$  orbital leading to dissociation into OH + H (photodissociation). Such dissociation can also be achieved by consecutive absorption of two 266 nm photons [589]. Absorption of two higher energy photons, at 200 nm, gives rise to a hydrated electron by  $H_2O + hv \rightarrow H_2O^+ + e^-_{aq}$  [1057]. Inelastic x-ray scattering studies find this far UV peak to be absent in liquid water [355], where the major peak is at about 56 nm. The infrared spectrum runs into microwave radiation at longer wavelengths. This interacts with the water dipole, moving the molecules backwards and forwards and so stretching and bending the hydrogen bonds, which generates heat. If the radiation is at too high a frequency ( $> 1000$  GHz,  $\lambda < 0.3$  mm), the molecules do not have time to react to the electromagnetic field changes and no heat is generated. If the radiation is at lower frequencies ( $< 1$  GHz,  $\lambda > 30$  cm), the molecules react to the electromagnetic field changes but so slowly that effectively no heat is generated. Pure water is almost totally transparent to such low frequency radiation. The maximum absorption varies to higher frequencies at higher temperatures when the weaker hydrogen bonding allows a quicker response to changes in the field [136]. Microwave ovens typically use radiation at 2.450 GHz ( $\lambda$  12.24 cm). More details on the response of water to microwave radiation are [available](#).

The reported structuring absorption of [sound](#) by water is not generally accepted.

<sup>a</sup> Dielectric studies showed an opposite effect with the absorbance at around  $200\text{ cm}^{-1}$  increasing with increasing temperature to about  $30^\circ\text{C}$  before reducing with increasing temperature due to hydrogen bond breakage [608]. The discrepancy may be due to additional relaxation processes detected by these dielectric studies in addition to the hydrogen bond stretching detected by infrared spectroscopy [819]. [[Back](#)]

<sup>b</sup> This band may be due to third overtone of the libration band, with the second overtone introducing asymmetry into the bend ( $\nu_2$ ) vibration [699b]. [[Back](#)]

c The sky is blue due to molecular light scattering, with neither tiny air-borne particles nor its small and variable content of gaseous water having significant effect [710]. [Back]

d This curve(s) has been generated using data for liquid and frozen water to give a continuous curve showing the main features. For exact data please consult the original references [130]. The absorption coefficient  $\mu_{a(\lambda)}$ , with units of  $\text{cm}^{-1}$ , at a particular wavelength ( $\lambda$ ) is given by the equation  $\frac{I}{I_0} = e^{-\mu_{a(\lambda)}l}$  where  $I$  is the transmitted intensity of the light,  $I_0$  is the incident intensity of the light and  $l$  is the path length (cm). The absorbance ( $A$ , in optical density units) is defined by the equation  $A = -\text{Log}_{10}\left(\frac{I}{I_0}\right)$ . The transmittance ( $T$ ) of a sample is defined by  $T = \left(\frac{I}{I_0}\right)$ . The molar extinction coefficient  $\epsilon_{(\lambda)}$ , with units  $\text{liters mole}^{-1} \text{cm}^{-1}$ , is defined by the equation  $A = \epsilon_{(\lambda)}c l$  where  $c$  is the molar concentration (= 55.345 M for liquid water at 25°C) and  $l$  is the path length (cm). Comparison of these definitions shows that  $A = \frac{\mu_{a(\lambda)}l}{2.303}$  and  $\epsilon_{(\lambda)} = \frac{\mu_{a(\lambda)}}{2.303c}$  (note that  $\log_e(10) = 2.302585$ ). [Back]

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[Site Index](#) | [Microwave effects](#) | [Water molecule](#) | [Magnetic effects](#) | [Notes](#)



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