Why Is Water Blue?

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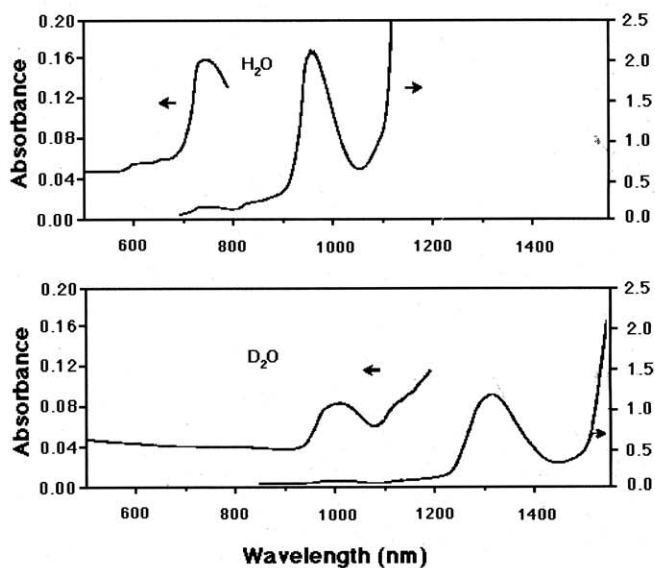Dartmouth College, Hanover, NH 03755

Often over the years, we have asked scientific colleagues why it is that water is blue. Common responses have included light scattering—after all the sky is blue—and coloration by dissolved impurities—Cu^{2+} has been a popular suggestion. However, the work described below demonstrates that water has an intrinsic color, and that this color has a unique origin. This intrinsic color is easy to see and has been seen by the authors in the Caribbean and Mediterranean Seas and in Colorado mountain lakes. Because the absorption that gives water its color is in the red end of the visible spectrum, one sees blue, the complementary color of red, when observing light that has passed through several meters of water. This color of water also can be seen in snow and ice as an intense blue color scattered back from deep holes in fresh snow. Blue to blue-green hues also are scattered back when light deeply penetrates frozen waterfalls and glaciers.

Water owes its intrinsic blueness to selective absorption in the red part of its visible spectrum. The absorbed photons promote transitions to high overtone and combination states of the nuclear motions of the molecule; i.e., to highly excited vibrations. To our knowledge the intrinsic blueness of water is the only example from nature in which color originates from vibrational transitions. Other materials owe their colors to the interaction of visible light with the electrons of the substances. Their colors may originate from resonant interactions between photons and matter such as absorption, emission, and selective reflection or from non-resonant processes such as Rayleigh scattering, interference, diffraction, or refraction, but in each case, the photons interact primarily or exclusively with electrons. The details of the mechanism by which water is vibrationally colored will be discussed in the paragraphs that follow.

Vibrational Transitions

Laboratory observation of the vibrational transitions that give water its color requires only simple equipment. The figure gives the visible and near IR spectrum of H_2O at room temperature recorded using a Perkin–Elmer Lambda 9 Spectrophotometer and a 10-cm quartz cell filled with "nanopure" water from an ion-exchange apparatus manufactured by Barnstead. Lower purity, distilled water gave an almost identical spectrum. The absorption below 700 nm in wavelength contributes to the color of water. This absorption consists of the short wavelength tail of a band centered at 760 nm and two weaker bands at 660 and 605 nm. The vibrational origin of this visible absorption of H_2O is demonstrated in the figure by the spectrum of D_2O recorded in the same 10-cm cell. D_2O is colorless, because all of its corresponding vibrational transitions are shifted to lower energy by the increase in isotope mass. For example, the H_2O band at 760 nm is shifted to approximately 1000 nm in D_2O (See the figure).

The blue color of water may be easily seen with the naked eye by looking through a long tube filled with purified water. We used a 3-m long by 4-cm diameter length of aluminum tubing with a Plexiglas window epoxied to one end of the tube. Ten or more observers each reported see-

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The upper spectrum is that for liquid H_2O in a 10-cm cell at room temperature; the lower spectrum is for D_2O under the same conditions. No cell was used in the reference beam of the spectrophotometer so that the "baseline" absorbance of approximately 0.04 originates in cell reflections.

ing a blue color when they looked through the tube and observed a sunlight-illuminated white paper placed below the vertically-suspended tube. This observation is in accord with the spectrum of H_2O recorded in the figure. For example, from the measured absorbance at 660 nm, the calculated transmission of a 3-m water-filled tube is 44%—a loss of red intensity that should be perceptible. Light transmitted through the empty cell was white. The large tube volume and a limited budget precluded checking to see if light transmitted through a D_2O-filled tube was indeed white, as expected.

Water is unique among the molecules of nature in its high concentration of OH bonds and in its plentiful supply. Most important, the OH symmetric (v_1) and antisymmetric (v_3) vibrational stretching fundamentals are at high enough energy [3650 cm^{-1} and 3755 cm^{-1}, respectively] (1) so that a four quantum overtone transition ($v_1 + 3v_3$) occurs at 14,318.77 cm^{-1} (698 nm), just at the red edge of the visible spectrum. As we shall see, these gas phase transition energies are all shifted to *lower* energy by the hydrogen bonding of liquid water.

Stretching Frequencies and Absorption Intensities

Because the absorption strength of the successive overtone transitions of water falls by a factor of 10 to 20 as the number of stretching quanta increases by unity (2), overtone transitions with more than five stretching quanta do not significantly contribute to the color of water. Of course if the OH stretch were perfectly harmonic, the strength of all overtones and combination bands would be zero. Thus, it is critical both that the OH potential is anharmonic and that the fundamental stretching frequencies are high

enough that overtones with only four and five stretching quanta can contribute to absorption intensity in the visible. D_2O is colorless, at least for path lengths on the order of meters, because a minimum of six stretching quanta would be required for any transition in the visible region.

Gas Phases versus Liquid Phases

It is interesting to compare the gas phase spectrum of water, for which all overtone and combination bands are assigned, with the liquid phase spectrum that appears to be less completely described with respect to the origin of infrared and visible vibrational bands. This is important in that it clarifies the role of hydrogen bonding in the liquid phase spectrum, a matter of some confusion in the several sources that address the question of why water is blue.

Note in the table that the liquid phase OH-stretching band centered at about 3400 cm^{-1} (3) is red shifted from the gas phase values of v_1 and v_3 by several hundred wavenumbers. This shift is primarily the result of hydrogen bonding in the liquid. The shift to lower energy induced by hydrogen bonding is seen perhaps most clearly in a comparison of the stretching frequencies observed for monomeric and dimeric water in a solid nitrogen matrix. Tursi and Nixon (4) confirmed earlier matrix isolation work by Van Thiel et al. (5) to establish that, while the monomer OH-stretching bands v_1 and v_3 were slightly red shifted (~ 25 cm^{-1}) from gas phase energies by the matrix, the frequency of the dimer OH stretch involved in a hydrogen bond was red shifted to 3547 cm^{-1}. That is 105 and 209 cm^{-1} below the gas phase values of v_1 and v_3, respectively. Hydrogen bonding shifts the overtone and combination band transitions to lower energy as well (see the table). In fact, each of the near-IR bands of liquid water shifts to higher energy as the temperature is raised (6). This has been attributed by several workers (6, 7) to the decreasing importance of hydrogen bonding with increasing temperature. As expected from such arguments the near IR absorption bands of ice are the most red shifted of all (6).

The assignment in the table of the four liquid-phase bands from 5000 to 11000 cm^{-1} seems almost certain and agrees with that of Nassau (8) and of Luck (6). We are convinced of the assignments by the work of Luck (6) in which the near-IR absorptions were observed in water at temper-

atures up to the critical point. As the temperature is increased, hydrogen bonding decreases in importance to the point that at 375 °C the liquid peaks are only an average of 80 cm^{-1} below the gas phase transitions of the table. Our assignment in the table of the higher energy liquid phase transitions from 600–800 nm is speculative and should not be taken too seriously. The main point is to show that the red absorption which gives rise to the blue color of liquid water can be ascribed plausibly to high energy vibrational overtone and combination bands which, like the other bands of the table, have been shifted to lower energy by hydrogen bonding. We also have measured H_2O spectra like those of the figure at 1 °C and at 51 °C. As the temperature is lowered, the band near 760 nm shifts to lower energy but also broadens enough to increase the intensity near 700 nm. However, the changes are small enough that the color of water should not vary significantly with temperature between 0 and 50 °C.

We are not the first to call attention to the vibrational origin of water's blue color. However, Nassau, in his generally excellent book (8), *The Physics and Chemistry of Color*, credits hydrogen bonding in water with strengthening the bonding and thus raising the frequency of high overtone and combination bands. Such frequency increases would shift H_2O monomer (gas phase) transitions from the near IR into the visible thus increasing the visible absorption of water. However, as we see from the table, hydrogen bonding causes the stretching frequencies of H_2O to shift to lower, not higher frequencies. Atkins, too, invokes hydrogen bonding as crucial to the visible color of water and ice (9). Instead, it appears to us that the hypothetical liquid without any hydrogen bonds still would be colored, perhaps even more intensely than is actual water. Dera, too, invokes vibrational overtones as the origin of the red absorption by water. His work is notable for its thorough compilation of visible spectra of water (10). Happily, the absorption coefficients that he tabulates for water sampled from around the globe show that the absorption seen in the figure is characteristic of most oceans. Pollution has not altered the color of the earth's great seas (10).

Still one may well ask, "Why when one looks *at* a body of water, not *through* it, does one often see a blue color?" Bohren (11) has answered that question in his highly recommended book, *Clouds in a Glass of Beer*. He makes it clear that any simple answer is bound to mislead. It turns out that contributions to the observed color are made both by reflected skylight and by the intrinsic absorption of water described above (11). Light scattering by suspended matter is required in order that the blue light produced by water's absorption can return to the surface and be observed. Such scattering also can shift the spectrum of the emerging photons toward the green, a color often seen when water laden with suspended particles is observed. Furthermore, as Bohren shows (11), the relative contribution of reflected skylight and the light scattered back from the depths is strongly dependent on observation angle.

The absorption spectrum of ice (6, 12) is similar to that of the liquid except that hydrogen bonding causes all peaks to shift to lower energy. An elegant description of the colors transmitted by snow and ice also has been given by Bohren (13). His paper should be consulted for the fascinating story of how multiple scattering combined with red light absorption in snow gives rise to a "vivid blueness" beneath snow's surface that exceeds in purity "that of the bluest sky". Bohren also discusses (13) how the larger grain sizes of bubbly ice allow deep penetration of incident light and a reflected hue that can vary from blue-green to blue depending on the color of the surface that underlies the ice.

Students usually are fascinated by the topic of color. Because the mechanism is unique, the story of the vibrational

Vibrational Tansitions of Gaseous and Liquid (20 °C) Water

Gas[a]	Assignment[a]	Liquid	Shift
3.6517	v_1	3.40[b]	
3.7558	v_3		
5.332	v_2+v_3	5.15[c]	0.18
7.2516	v_1+v_3	6.90[c]	0.35
8.807	$v_1+v_2+v_3$	8.40[c]	0.41
10.613	$2v_1+v_3$	10.3[c]	0.31
13.831	$3v_1+v_3$	13.16(760 nm)	0.67
14.319	v_1+3v_3	13.51(740 nm)[s]	0.81
15.348	$3v_1+v_2+v_3$	15.15(660 nm)	0.20
15.832	$v_1+v_2+3v_3$	15.15(660 nm)	0.68
16.822	$3v_3+2v_2+v_1$		
16.899	$4v_4+v_1$	16.53(605 nm)	0.37

[a] is Ref. 1;

[b] is Ref. 3;

[c] is Ref. 2; s=shoulder; All liquid phase assignments of gas phase transitions which lie above 10,613 cm^{-1} are based on the figure and are speculative.

Transition energies and shift are in units of 10^3cm^{-1}. Transitions that involve excitations of the bending mode v_2 are omitted except when stretch plus bend combination bands appear in the liquid spectrum. Also omitted are several other weak gas phase transitions that do not appear to give rise to structure in the liquid spectrum.

origin of the color of water and ice should attract their curious minds.

Acknowledgment

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