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SPECTROSCOPY OF HEAVY WATER & ITS EFFECTON ENVIRONMENT

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ABSTRACT

The relative abundance of the heavy water isotopologue HDO provides a deeper insight into the atmospheric hydrological cycle. The Scanning Imaging Absorption spectrometer for Atmospheric Cartography (SCIAMACHY) allows for global retrievals of the ratio HDO/H_2O in the 2.3-micron wavelength range. However, the spectroscopy of water lines in this region remains a large source of uncertainty for these retrievals. We therefore evaluate and improve the water spectroscopy in the range 4174–4300 cm^{-1} and test if this reduces systematic uncertainties in the SCIAMACHY retrievals of HDO/H_2O. We use a laboratory spectrum of water vapour to fit line intensity, air broadening and wavelength shift parameters. The improved spectroscopy is tested on a series of ground-based high resolution FTS spectra as well as on SCIAMACHY retrievals of H_2O and the ratio HDO/H_2O. We find that the improved spectroscopy leads to lower residuals in the FTS spectra compared to HITRAN 2008 and Jenouvrier et al. (2007) spectroscopy, and the retrievals become more robust against changes in the retrieval window. For both the FTS and SCIAMACHY measurements, the retrieved total H_2O columns decrease by 2–4% and we find a negative shift of the HDO/H_2O ratio, which for SCIAMACHY is partly compensated by changes in the retrieval setup and calibration software. The updated SCIAMACHY HDO/H_2O product shows somewhat steeper latitudinal and temporal gradients and a steeper Rayleigh distillation curve, strengthening previous conclusions that current isotope-enabled general circulation models underestimate the variability in the near-surface HDO/H_2O ratio.

INTRODUCTION

Heavy water, formally called deuterium oxide or ^2H_2O or D_2O, is a form of water that contains a larger than normal amount of the hydrogen isotope deuterium, (also known as "heavy hydrogen") rather than the common hydrogen-1 isotope that makes up most of the hydrogen in normal water. Therefore, some or most of the hydrogen atoms in heavy water contain a neutron, causing each hydrogen atom to be about twice as heavy as a normal hydrogen atom (although the weight of the water molecules is not as substantially affected, since about 89% of the molecular weight resides in the unaffected oxygen atom). The increased weight of the hydrogen in the water thus makes it slightly more dense. The colloquial term *heavy water* is often also used to refer a highly enriched water mixture that contains mostly deuterium oxide but also contains some ordinary water molecules as well: for instance, heavy water used in CANDU reactors is 99.75% enriched by hydrogen atom-fraction, meaning that 99.75% of the hydrogen atoms are of the heavy type. In comparison, in ordinary water, which is the "ordinary water" used for a deuterium standard on Earth, there are only about 156 deuterium atoms per million hydrogen atoms. Heavy water is not radioactive. In its pure form, it has a density about 11% greater than water, but otherwise, is physically and chemically similar. Nevertheless, the various differences in deuterium-containing water (especially affecting the biological properties) are larger than in any other commonly occurring isotope-substituted compound because deuterium is unique among heavy stable isotopes in being twice as heavy as the lightest isotope. This difference increases the strength of water's hydrogen-oxygen bonds, and this in turn is enough to cause differences that are important to some biochemical reactions. The human body naturally contains deuterium equivalent to about five grams of heavy water, which is harmless. When a large fraction of water (> 50%) in higher organisms is replaced by heavy water, the result is cell dysfunction and death. Heavy water was first produced in 1932, a few months after the discovery of deuterium. With the discovery of nuclear fission in late 1938, and the need for a neutron moderator that captured few neutrons, heavy water became a component of early nuclear energy. Since then, heavy water has been an essential component in some types of reactor, both those that generate power and those designed to produce isotopes for nuclear weapons, such as plutonium-239. These heavy water reactors have the advantage of being able to run on natural uranium without the use of graphite moderators which can pose radiological and dust explosion hazards in the decommissioning phase. Most modern reactors use enriched uranium with normal "light water" (H_2O) as the moderator.

REVIEW OF LITERATURE

Harold Urey discovered the isotope deuterium in 1931 and was later able to concentrate it in water. Urey's mentor Gilbert Newton Lewis isolated the first sample of pure heavy water by electrolysis in 1933. George de Hevesy and Hoffer used heavy water in 1934 in one of the first biological tracer experiments, to estimate the rate of turnover of water in the human body. The history of large-quantity production and use of heavy water in early nuclear experiments is given below. Emilian Bratu and Otto Redlich studied the autodissociation of heavy water in 1934 Different isotopes of chemical elements have slightly different chemical behaviors, but for most elements the differences are far too small to use, or even detect. For hydrogen, however, this is not true. The larger chemical isotope-effects seen between protium (light hydrogen) versus deuterium and tritium manifest because bond energies in chemistry are determined in quantum mechanics by equations in which the quantity of reduced mass of the nucleus and electrons appears. This quantity is altered in heavy-hydrogen compounds (of which deuterium oxide is the most common and familiar) more than for heavy-isotope substitution in other chemical elements. This isotope effect of heavy hydrogen is magnified further in biological systems, which are very sensitive to small changes in the solvent properties of water. Heavy water is the only known chemical substance that affects the period of circadian oscillations, consistently increasing the length of each cycle. The effect is seen in unicellular organisms, green plants, isopods, insects, birds, mice, and hamsters. The mechanism is unknown. To perform their tasks, enzymes rely on their finely tuned networks of hydrogen bonds, both in the active center with their substrates, and outside the active center, to stabilize their tertiary structures. As a hydrogen bond with deuterium is slightly stronger[16] than one involving ordinary hydrogen, in a highly deuterated environment, some normal reactions in cells are disrupted. Particularly hard-hit by heavy water are the delicate assemblies of mitotic spindle formation necessary for cell division in eukaryotes. Plants stop growing and seeds do not germinate when given only heavy water, because heavy water stops eukaryotic cell division The deuterium cell is larger and a modification of the direction of division. The cell membrane also changes, and it reacts first to the impact of heavy water. In 1972 it was demonstrated that an increase in the percentage content of deuterium in water reduces plant growth. Research conducted on the growth of prokaryote microorganisms in artificial conditions of a heavy hydrogen environment showed that in this environment, all the hydrogen atoms of water could be replaced with deuterium Experiments showed that bacteria can live in 98% heavy water. However, all concentrations over 50% of deuterium in the water molecules were found to kill plants.It has been proposed that low doses of heavy water can slow the aging process by helping the body resist oxidative damage via the isotope effect A team at the Institute for the Biology of Ageing, located in Moscow, conducted an experiment to determine the effect of heavy water on longevity using fruit flies and found that while large amounts were deadly, smaller quantities increased lifespans by up to 30%. Experiments in mice, rats, and dogs have shown that a degree of 25% deuteration causes (sometimes irreversible) sterility, because neither gametes nor zygotes can develop. High concentrations of heavy water (90%) rapidly kill fish, tadpoles, flatworms, and *Drosophila*. Mammals, such as rats, given heavy water to drink die after a week, at a time when their body water approaches about 50% deuteration.

RESEARCH METHODOLOGY

On 19 November 1942, a pair of Royal Air Force Halifax bombers shouldered their way through thick winter clouds over Norway with troop-carrying assault gliders in tow. Inside each glider a payload of professional saboteurs from the 1st British Airborne Division weathered a rough ride as the planes approached their intended landing site on frozen lake Møsvatn. Somewhere in the snow-encased hills below, a team of Norwegian commandos vigilantly Scientists at Vemork first observed the curious heavy-water in 1934 when it appeared as a by-product of their revised ammonia production process. Physically and chemically the substance is similar to ordinary water, but while the hydrogen atoms in normal H_2O consist of one proton and one electron, many of the hydrogen atoms in heavy-water have the added weight of a neutron-- an isotope known as *deuterium*. This deuterium oxide (D_2O) does exist in water naturally, though its ratio is normally only about one part in 41 million, so it had not been previously observed in significant quantities. For eight years Vemork's scientist had been collecting the exotic liquid for scientific scrutiny, supplying samples to the world's researchers for basic experiments. The Nazis' interest, however, was more considerably more sinister. In the late 1930s a group of German physicists discovered that certain rare isotopes of uranium are fissile, meaning that their nuclei become unstable and split when they absorb an extra neutron. The nucleus shatters into two smaller nuclei-- which repel one another with great energy due to their mutually repulsive electric charges-- and shrapnel consisting of fast-moving free neutrons. Soon scientists realized that a chain-reaction would be possible inside a clump of fissionable material since the neutrons spawned during one fission could trigger subsequent fissions, and those would trigger more fissions, and so on. Depending on the conditions, this could produce a long-lived source of heat and neutrons, or a short-lived source of exploding and death. They also speculated that a self-sustaining chain reaction would be easier to maintain if they could identify a substance able slow down the loose neutrons to increase their chances of being absorbed. Frozen heavy-water in ordinary H20 The nuclear Nazis identified Norway's heavy-water as one of the best candidates to act as this *neutron moderator*, so when German forces invaded in 1940 the Vemork plant was an asset they were quick to snatch. Under tightened security, the German scientists doubled the heavy-water production capacity and began shipping barrels of the material back to the weapons laboratories in Berlin. The Norwegian civilian workers knew nothing of nuclear bombs or neutron moderators, but the Nazis' conspicuous interest in the substance prompted members of the resistance to report the activity to British intelligence. By 1942 the Allied leaders were certain that the heavy water was a critical component in Hitler's effort to produce an atomic weapon. Such neutron moderators were not necessary in atomic bombs, but the German physicists hoped to use heavy-water to moderate a sustained reaction within their stash of rare uranium-235. They could then expose nuggets of the most common uranium isotope (uranium-238) to the slow neutrons spewing out of the reactor, allowing some of the uranium nuclei to slurp up an extra neutron to become uranium-239. U-239 atoms tend to undergo *beta decay* a couple times over the course of a few days, finally resulting in weapons-grade plutonium-239. The Allies could not sit idly by as Hitler's henchmen made progress in nuclear weaponry, otherwise the war was sure to come to an abrupt and disagreeable end. The British Royal Air Force considered a nighttime bombing raid on the Vemork to be "unrealistic," so a covert ground assault was mounted. On 19 November 1942, thirty Royal Engineers crowded into a pair of troop gliders and rode to the frozen landscape of Norway towed behind Halifax bombers. In the mountains near the power plant, an advance team of Norwegian commandos waited near the landing zone while the planes struggled through the soupy skies. As the drone of aircraft engines crept over the horizon towards Jens Anton Paulsson and his three men, there was a dull explosion in the distance. Once its echoes faded only one aircraft could be heard. One of the Halifax bombers had struck a cloud-obscured mountain. The glider pilot-- who had managed to cast off from his ill-fated tug at the last moment-- executed the most graceful crash he could give the mountainous terrain. The remaining airplane circled the area with its own glider in tow as the crew struggled fruitlessly to contact the landing beacon. Eventually they were forced to give up due to low fuel, but as the bomber set off towards home its tow line broke and sent the second glider diving into the snowy hills.

RESULT & CONCLUSION

It displays the mass-selected R2PI spectra of the hydrated saccharides, a- and b-PhMan$(D2O), recorded in each of their parent ion mass channels. The spectra are quite distinct and only one of them shows any evidence of cluster ion fragmentation: the R2PI spectrum of the b-di-hydrate also appears strongly in the singly hydrated ion channel but, intriguingly, this does not occur in the corresponding a-di-hydrate. The anomeric effect in micro solvated D-mannose has been explored and directly exposed, through an investigation of the vibrational spectroscopy of the doubly and triply hydrated a and b anomers of phenyl D-mannopyranoside, isolated under molecular beam conditions in the gas phase. The investigation has been greatly aided by the simple experimental trick of substitutingD2O forH2O, which allows the (OH) vibrational bands associated with the saccharide to be separated from the (OD) bands associated with the bound water molecules. Subtle differences in the vibrational signatures of the hydrated a and b anomers can be interpreted in the light of complementary density functional theoretical calculations and a natural bond orbital analysis. The two singly hydrated anomers have identical structures, accessed in the b anomer through a change in the conformation of the monosaccharide, and the bound water molecule is located in the favoured water pocket at the 4,6 site. In the doubly hydrated anomers, the two water molecules again occupy the same template, bound on each side of the hydroxymethyl group, which places the additional W2 molecule at a site close to the anomeric region of the saccharide—but their structures, while similar, are not identical. The key structural change is mediated by changes consistent with 'lone pair repulsion' between the oxygen atomin the pyranose ring (O5) and the neighbouring water molecule. The extra water molecule thus acts as a remarkably sensitive 'spy', free from environmental influences and able to sense and expose subtle stereoelectronic changes through the resulting changes in its hydrogen-bonded interaction with the substrate. Similar effects appear to contribute to a change in the structure of the hydrogen bonded 'hydration crown' lying above the hydrophilic face of the carbohydrate, displayed in the triply hydrated anomers. These studies now provide precise structural data for the differences in solvation caused by the anomeric effect. They are likely to contribute to the striking differences between anomers found in nature, for example, between cellulose (a b1,4Glc polymer) and starch (an a1,4Glc polymer). The a- and b- anomers of phenyl D- mannopyranoside were synthesized following methods described previously. Their hydrated (D2O) complexes were generated in the gas phase using a combination of pulsed laser ablation and molecular beam procedures. Ground powdered samples of the carbohydrate were thoroughly mixed with graphite powder (20% graphite:80% sample, w/w), deposited as a thin uniform surface layer on a graphite substrate, and placed in a vacuum chamber close to and just below the exit of a pulsed, cylindrical nozzle expansion valve (0.8 mm diameter).

The carbohydrates, desorbed by laser evaporation from the surface, were entrained and cooled in an expanding argon jet (4 bar backing pressure) seeded with D2O, before passing into the detection chamber through a 2 mm diameter skimmer to create a collimated molecular beam. This was crossed by pulsed tunable UV and IR laser beams in the extraction region of a linear, Wiley-McLaren time-of- flight mass spectrometer (R. M. Jordan).

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