

Contrary to common belief, the greenhouse effect may have more to do with water in our atmosphere than gasses such as carbon dioxide

The climatic effects of water vapour

Ahilleas Maurellis and Jonathan Tennyson

EXTREME variations in local weather and the seasons make it easy for people to mutter “greenhouse effect”, and blame everything on carbon dioxide. Along with other man-made gases, such as methane, carbon dioxide has received a bad press for many years and is uniformly cited as the major cause of the greenhouse effect. This is simply not correct. While increases in carbon dioxide may be the source of an enhanced greenhouse effect, and therefore global warming, the role of the most vital molecule in our atmosphere – water – is rarely discussed. Indeed, water barely rates a mention in the hundreds of pages of the 2001 report by the Intergovernmental Panel on Climate Change.

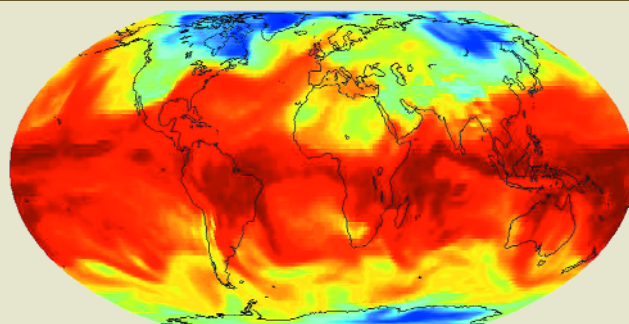
Many aspects of the seemingly simple water molecule conspire to make it difficult to model its effect on our climate. Unlike most other atmospheric gases, the distribution of water in the atmosphere varies strongly with time, location and altitude (figure 1). Water is also unique among atmospheric molecules because it changes phase at terrestrial temperatures. This means that it can transfer energy from its frozen form at the poles to its liquid and vapour forms in the atmosphere. Once in the atmosphere, water moves with the winds and can even diffuse up to the stratosphere, where it is responsible for destroying the ultraviolet-shielding ozone layer.

The atmosphere plays a crucial role in the Earth’s radiation budget because it absorbs both the incoming radiation from the Sun and the outgoing radiation that is reflected from the planet’s surface. However, the radiation in each of these processes has very different wavelengths. The Sun radiates approximately as a black body with a temperature of 5800 K, which peaks in the optical region at a wavelength of about 0.6 μm . The reflected radiation profile, on the other hand, is much closer to a black body at a temperature of 275 K, and has a peak at much longer infrared wavelengths (about 11 μm). The physical processes that lead to the absorption of radiation in the two regions are different, but water vapour plays the dominant role in both.

Balancing the books

Physicists have been modelling the Earth’s atmosphere for over a century, and we have built up a very detailed understanding of the key processes that are involved in the global energy budget (figure 2). For example, it is now well estab-

1 Water in the atmosphere



The distribution of water in the atmosphere varies strongly with time, location and height, which makes it difficult to model. This image shows the distribution of water vapour in the Earth’s atmosphere using data from September 1996. The humid tropics (red) contain almost 100 times more water vapour than the dry poles (blue).

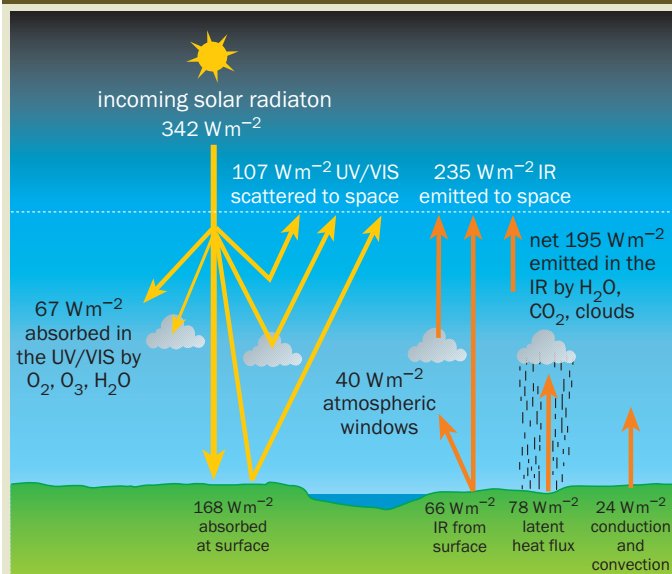
lished that the top of the Earth’s atmosphere receives a surface-averaged energy input from the Sun of 342 W m^{-2} . This is calculated by knowing the amount of energy that is radiated by the Sun and the angle that the Earth subtends. If the incoming and outgoing radiation is not equal then the global energy budget does not balance and the temperature of the planet will change until a new balance is established. What is feared is that a build-up of greenhouse gases is causing an increase in the absorption of the outgoing, infrared radiation.

Satellite measurements show that 235 W m^{-2} of incoming solar radiation is absorbed by the Earth, but the latest models and measurements suggest that the atmosphere is responsible for just 67 W m^{-2} of this amount. The rest is absorbed by the ground and by the oceans, which play a key role in the energy budget due to their large heat capacity and their ability to store carbon dioxide, and, of course, water vapour.

The greenhouse effect is precisely the difference between the long-wave radiation that is emitted by the Earth’s surface and the upward thermal radiation that leaves the tropopause – the upper boundary of the turbulent portion of the atmosphere that we all inhabit. The greenhouse effect is about 146 W m^{-2} in clear skies and some 30 W m^{-2} higher under cloud cover.

There are a number of popular misconceptions about the

2 The global energy budget



The global energy balance of the Earth–atmosphere system. Radiation that is absorbed by the atmosphere in the ultraviolet (UV) and visible (VIS) regions of the spectrum contributes to the emission in the infrared region (IR). The incoming solar radiation is either reflected directly back into space, absorbed by the atmosphere or absorbed by the Earth’s surface. The 67 W m^{-2} ultraviolet–visible absorption that is due to atmospheric trace gases, such as water, also translates into infrared emission, which combines with the infrared surface heat to emerge as some 195 W m^{-2} . However, the measured atmospheric absorption is up to 30 W m^{-2} higher than models predict, and this is known as the absorption anomaly.

greenhouse effect, notably that it is a bad thing. On the contrary, the greenhouse effect is a significant factor in making the Earth habitable. Without it the average temperature on Earth would be lowered by about 30 K, which would make most of the planet’s surface decidedly chilly. Furthermore, it is the water vapour in the lower 10 km or so of the atmosphere, rather than man-made carbon-dioxide emissions, that contributes most to this warming effect.

The absorption of light by molecules in the atmosphere generally results in two basic molecular processes: bound–free and bound–bound transitions. Bound–free transitions take place in the more energetic ultraviolet region of the spectrum and cause the molecules to break up. In bound–bound transitions, which occur at longer wavelengths, the molecules jump from some combination of rotational and vibrational states to another, which produces a very distinct “signature” (figure 3). It is therefore very easy to identify which atmospheric absorbers are at work, although it is much more difficult to work out the actual numbers. Nevertheless, large databases that list all the known molecular transitions and their associated properties have been compiled. The most widely used is the high-resolution transmission molecular absorption database (HITRAN), which has been developed over many years by Larry Rothman, who is now at the Harvard-Smithsonian Center for Astrophysics in Cambridge in the US.

But when the absorption values in the HITRAN database are used in model-atmosphere calculations, the results are disturbing. For clear skies, the models predict that the atmosphere absorbs much less sunlight than is measured by a variety of satellite and aircraft. The difference between the predictions and the measurements can be as large as

30 W m^{-2} . (see “Radiation budget is called to account” by A Maurellis *Physics World* November 2001 pp22–23). This problem has become known as the absorption anomaly. And there are even worse problems in understanding absorption models when the sky is cloudy.

Not all models underestimate the amount of atmospheric absorption because some physicists choose to add extra absorption to their models to mop up the surplus radiation. However, the physical cause of the missing clear-sky absorption and its exact wavelength distribution remain unresolved, and a source of fertile speculation. Everyone’s favourite molecule is always a candidate.

Our favourite molecule is water. Water vapour is responsible for 70% of the known absorption of incoming sunlight, particularly in the infrared region. Indeed, ask any infrared astronomer about which regions of the spectrum provide the best views and you will get a list of the wavelengths where water does *not* absorb – the so-called atmospheric windows. After all, there have to be some pretty strong reasons to brave the inhospitable climate of Antarctica to build the South Pole Telescope, as US astronomers have recently undertaken. Water absorption bands are also present in the optical region and extend all the way to the ultraviolet, although they are less strong at shorter wavelengths. The precise effect of these absorption bands is hard to determine, despite the best efforts of many talented and dedicated scientists.

An incredible lightness of being

Air is largely composed of the diatomic molecules nitrogen and oxygen. So why is the transport of light through our atmosphere dominated by trace amounts of triatomic molecules such as water, carbon dioxide and ozone? After all, these molecules are only present above our heads at a level of about one part in 100 000.

The answer lies in the physics of the individual molecules involved. Molecules absorb radiation at characteristic wavelengths that excite one or more of their rotational, vibrational or electronic degrees of freedom. The probability that absorption occurs in a particular molecule gives the intensity of each line in the absorption spectrum. The intensities of these spectral lines depend on the net distribution of electronic charge within the molecule via dipole moments, which describe how the molecule responds to an applied electric field – such as that of an incoming light beam.

Symmetric linear molecules, such as N_2 , O_2 and even CO_2 , have symmetric charge distributions and therefore they do not have a permanent dipole moment. Furthermore, dipole moments cannot be induced in symmetric diatomic molecules by vibrational or rotational excitation because this does not change their topology. N_2 and O_2 can therefore only absorb light through electronic excitation. There are some important oxygen absorption bands that are associated with electronic excitation in the visible portion of the spectrum (see figure 3), but these do not extend over many wavelengths and so do not block major amounts of radiation. This means that oxygen accounts for just 2% of the atmospheric absorption of incoming sunlight, and nitrogen accounts for essentially none.

The water molecule, on the other hand, has a bent triangular structure, as does ozone – which is not as symmetric as the formula O_3 might suggest. Both of these molecules therefore possess permanent dipole moments, which means that they can absorb very long wavelength light that excites their rota-

tional states. The asymmetry of water and ozone molecules causes the moments of inertia that govern the quanta of rotational motion to be different in each spatial direction (see figure 4). These “asymmetric top” molecules have complicated energy levels, which interact with light to produce dense spectral lines that contain little obvious structure.

More importantly for climatic issues, the vibrational degrees of freedom in water, ozone and carbon-dioxide molecules can absorb light in the infrared region. In the case of carbon dioxide it is these vibrations that break the symmetry of the molecule and enable it to become excited by atmospheric radiation. O_3 , like its near relative O_2 , has a number of low-lying electronic states that absorb light in the near ultraviolet. Unlike O_2 , however, the extensive vibrational and rotational structure of ozone means that its electronic transitions absorb radiation over a wide range of wavelengths. But what is so special about water that makes its absorptions extend all the way from the far infrared to the near ultraviolet?

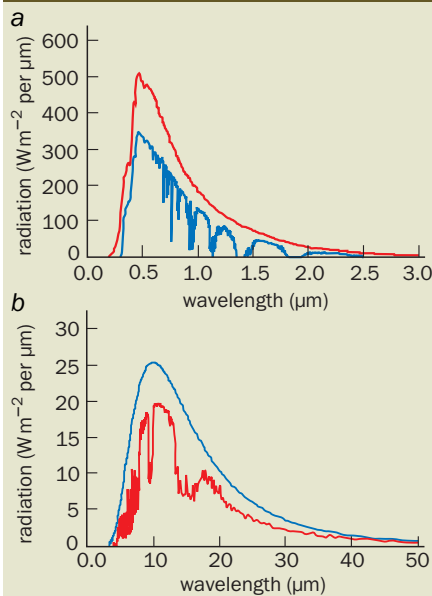
The simplest answer to this is that water, unlike the other triatomic species, contains two atoms of hydrogen. The presence of hydrogen atoms has two important effects. When a water molecule rotates about its centre-of-mass – which is near the oxygen atom – it does so with small moments of inertia. This leads to a very wide-ranging rotational structure that causes absorption bands for all types of transitions to extend over large regions of the spectrum. Furthermore, the vibrational motions of water have a large amplitude because hydrogen atoms are very light. As a result, water does not vibrate as a simple harmonic oscillator – as most molecules do – and its vibrational transitions do not obey the general harmonic-selection rule. The only transitions allowed by this rule are those in which a vibrational quantum number changes by a single quantum. For water, transitions that involve changes of up to eight vibrational quanta are atmospherically important, which means that the water-vapour spectrum covers a large range of wavelengths and line intensities, and is generally very complex (figure 5).

Water, water on the wall, who is the fairest of them all?

The vibration–rotation spectrum of water has been the subject of numerous laboratory studies over many decades. Despite their atmospheric importance, the line intensities of water in the near-infrared and visible regions of the spectrum are actually very weak. To measure the line spectra, researchers shine light over a large range of wavelengths through a very long column of water. This simulates the several kilometres of water vapour that solar radiation traverses before it reaches the Earth’s surface.

These long pathlengths are achieved in the laboratory by

3 Atmospheric absorption



Water in the atmosphere absorbs both incoming ultraviolet radiation from the Sun (a) and outgoing infrared radiation from the Earth (b). The red line in (a) and the blue line in (b) show the black-body spectrum that would be seen if there was no atmosphere. Note that the scales on each graph are different, indicating the different wavelengths of the incoming and outgoing radiation. The dominant absorption bands (dips) are due to water vapour, carbon dioxide and ozone in the atmosphere, but water dominates throughout the spectral range and is the cause of almost all the absorption bands seen in (a) and (b). In the outgoing radiation from the Earth, however, the main absorption band is due to carbon dioxide at about 15 μm . This is one of the mechanisms by which the surface of the Earth remains warm.

shining light through relatively short tubes – up to 50 m long – that have high reflectivity mirrors at their ends so that the light passes through the tube many times. Using this idea it has been possible to observe line intensities from strong transitions as well as numerous signatures of weak absorptions. High-resolution molecular spectroscopy has no difficulty in accurately measuring the wavelength of the spectral lines, but obtaining reliable measurements of the intensity of the lines – which tell us how much radiation is absorbed – presents much more of a challenge.

Water is also a nasty molecule to work with. Not because it is dangerous or attacks the experiment, but because its concentration is difficult to control. It forms droplets, it sticks to the walls of the tubes, it behaves unpredictably, and it does not mix properly with other gases. It is also present in the air in variable quantities, which makes it difficult to perform control experiments. Worse still, the absorption spectrum of water displays a huge dynamic range. Strong lines that are totally saturated (fully absorbing) in the atmosphere are close to very weak absorptions that must also be considered in any complete atmospheric model. Indeed, the individual dependence on the wavelength of light of these strong absorption lines is an important issue for atmospheric models.

Experiments that were performed by

Roland Schermaul and the late Richard Learner at Imperial College in London in 2001 have cast previous measurements of the absorption spectrum of water into considerable doubt. The study was motivated by the European Space Agency (ESA), which was concerned that the uncertainty in water-vapour data was preventing important information on trace molecules in the atmosphere from being obtained. Schermaul and co-workers used the Molecular Spectroscopy Facility at the Rutherford Appleton Laboratory in the UK to study the absorption of light by water vapour in air at wavelengths that varied from the near infrared to the orange. They found that the strong spectral lines absorbed significantly more light – between 5% and 25% – than previous laboratory measurements had suggested. This conclusion was given partial support by first-principle quantum-mechanical calculations, which can be used to estimate the strength of these absorptions.

In a parallel study, Schermaul and co-workers also measured the absorption of light by water vapour in an attempt to identify many of the weaker absorption lines that were predicted to be present in the spectrum (see figure 5). Similar studies were performed by Michel Carleer and co-workers from the Université Libre de Bruxelles in Belgium in 2002, who made measurements at shorter wavelengths that extended all the way into the ultraviolet – where the absorption lines of water are all weak.

These measurements were put into atmospheric models by Joanna Haigh's group at Imperial College to find out if they could explain the absorption anomaly. When the strength of the strong water absorption lines was increased in the model, the absorption of incoming sunlight rose by about 8 W m^{-2} . This increased by a further 3 W m^{-2} when the weak line parameters that were measured by Schermaul and co-workers were included. Together these increases represent about half of the absorption anomaly. Unfortunately, however, the situation is not quite this straightforward.

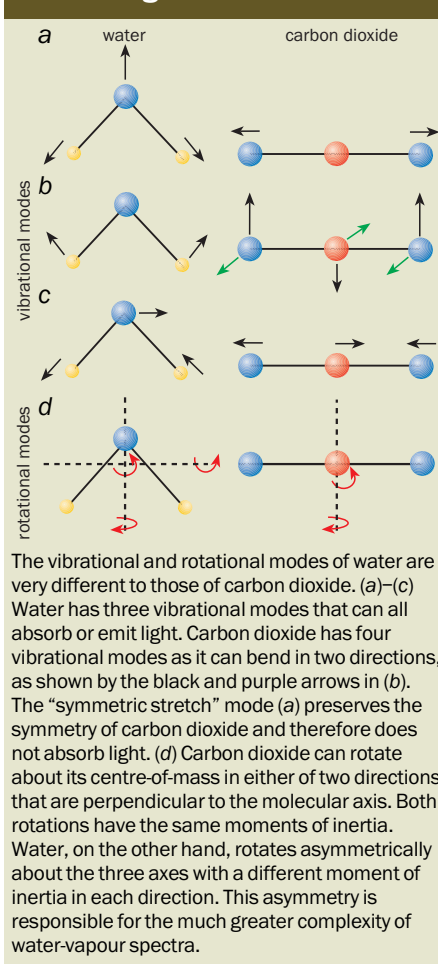
The increased absorption due to the weak water lines is generally accepted. Indeed, further increases are to be anticipated once the new, shorter-wavelength data from Carleer's team are also included in the models. However, other experiments, such as those performed by Linda Brown and colleagues from the Jet Propulsion Laboratory in Pasadena that were reported in 2002, find significantly smaller increases in the strength of absorption by the strong lines. This issue remains unresolved, although calculations of the vibration-rotation spectrum of water might be able to shed light on it in the near future. Quantum-mechanical calculations have become essential for interpreting the results from experiments, especially for assigning individual observed lines to transitions between a particular pair of energy levels. Calculations can also provide a complete set of transitions that allow for even the weakest lines. The 30 000 or so water absorption lines that are listed in the HITRAN database, for example, can be supplemented by about one billion water transitions that have been computed in a separate attempt to model the steam in the atmospheres of dwarf stars (see Jones *et al.* in further reading).

The spectroscopic data that are required to model long-wave atmospheric absorptions are generally well characterized. When these data are put into atmospheric models, water turns out to be responsible for about 60% of the greenhouse effect, while the much-reviled carbon-dioxide molecule accounts for just 26%. Ozone accounts for 8%, and methane and nitrous oxide – the atmospheric concentrations of which have been increased by human activity – contribute a further 8% to the greenhouse effect.

Should we ban dihydrogen monoxide?

We should not pretend that the effects of carbon dioxide are unimportant in the greenhouse effect. While the atmosphere has always contained a significant amount of water vapour, it is the apparent increase in atmospheric carbon dioxide since the period of industrialization that is causing so much concern. It turns out that typical abundances of carbon dioxide are sufficient to make most of its absorption bands relatively opaque (see figure 3). Because the strong absorption bands are saturated, adding more carbon dioxide to the atmosphere

4 Vibrating molecules



increases its absorptions logarithmically rather than linearly – a fact that is recognized by the Intergovernmental Panel on Climate Change.

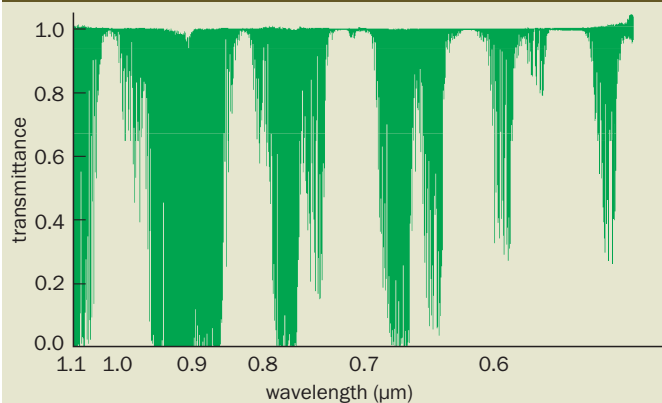
The concentration of water vapour in the atmosphere is strongly related to temperature, as can be seen in figure 1. It might therefore appear that an increased greenhouse effect, which causes the atmosphere to get warmer, would also lead to more water vapour in the atmosphere. This would result in a positive-feedback system that causes the Earth to become increasingly warmer. However, as is often the case with atmospheric processes, the situation is not quite this simple. Water vapour in the atmosphere can change phase, which leads to more clouds, and greater cloud cover means that more sunlight is reflected straight out of the atmosphere. Crude calculations suggest that the two effects approximately balance each other, and that water vapour does not have a strong feedback mechanism in the Earth's climate.

We have tried to outline some of the unresolved issues concerning water in the atmosphere. But there are others. For example, it is well known that at low temperature pairs of water molecules will stick together to form a weakly bound molecule known as a dimer. The absorption properties of the water dimer at visible wavelengths will be different from those of a single water molecule, but these remain to be characterized. Furthermore, it has so far proved impossible to determine the proportion of atmospheric water molecules that are present as dimers in either laboratory or atmospheric measurements. And we have not even dared to discuss the many problems in understanding clouds. Clouds are highly variable in their make-up, distribution and size. They contain aerosols and mini droplets of water vapour, which have spectroscopic properties that are even more uncertain than those of normal water vapour.

Another problem is that there are few data that tell us about the amount of water vapour in the atmosphere over history, which makes it difficult to determine the climatic effects from long-term changes in the atmosphere's water-vapour content. Fortunately, ESA's environmental satellite ENVISAT is now able to provide global coverage, and measure water-vapour signatures in the visible and near-infrared regions. Using complex mathematical techniques, the absorption spectra that are measured by satellites such as ENVISAT can be used to determine water-vapour columns, provided that accurate water-vapour spectroscopy is available.

A complete solution to the various problems that are associated with water absorption can only be obtained by constructing an accurate and comprehensive theoretical model of the spectrum of water. A significant step in this direction was taken in the last few months by Oleg Polyansky and co-

5 Water absorption spectrum



A laboratory spectrum showing some of the thousands of absorptions of light that can take place in water vapour. The spectrum extends from the near infrared (left) almost to the green. At long wavelengths the absorption is saturated, but it becomes less so at shorter wavelengths. The band structure reflects the various ways in which water molecules can absorb light through their vibrational and rotational degrees of freedom. This spectrum was obtained by Roland Schermaul and co-workers using the Molecular Spectroscopy Facility at the Rutherford Appleton Laboratory.

workers at University College London. They showed that a combination of advanced quantum-mechanical calculations and high-performance computing can be used to predict the positions of water spectra with an accuracy that approaches that from experiments. These calculations included the effects of special relativity, quantum electrodynamics and the coupled motions of electrons and nuclei, which were generally neglected in previous studies. The team is currently trying to improve the accuracy of these calculations, and to obtain similar accuracies for the intensity of the absorption lines.

It is clear that the absorption of radiation by water vapour determines many characteristics of our atmosphere. While we would not try to provoke any worldwide movement that was aimed at suppressing water emissions, it would seem that the climatic role of water does not receive the general attention it deserves.

Further reading

- P Bernath 2002 The spectroscopy of water vapour: experiment, theory and applications *Chem. Phys.* **4** 1501–1509
- H Jones *et al.* 2002 Spectral analysis of water vapour in cool stars *Mon. Not. R. Astron. Soc.* **330** 675–684
- J T Kiehl and K E Trenberth 1997 Earth's annual mean global energy budget *Bull. Am. Meteorol. Soc.* **78** 197–208
- G Marsh 2001 *A Global Warming Primer* National Center for Public Policy Research Policy Analysis Report No 361
- O Polyansky *et al.* 2003 High-accuracy *ab initio* rotation–vibration transitions for water *Science* **299** 539–542
- J Tennyson and O L Polyansky 1998 Water on the Sun: the Sun yields more secrets to spectroscopy *Contemporary Phys.* **39** 283–294

Link

HITRAN database: www.hitran.com

Ahilleas Maurellis is in the Earth-Oriented Sciences Division of the SRON National Institute for Space Research, Sorbonnelaan 2, 3584 CA Utrecht, the Netherlands, e-mail a.n.maurellis@sron.nl. **Jonathan Tennyson** is head of the Atomic, Molecular, Optical and Positron Physics group at University College London, Gower Street, London WC1E 6BT, UK, e-mail j.tennyson@ucl.ac.uk