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NEWS

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Water dimers detected in atmospheric conditions

Physicists in Russia are the first to detect water dimers – bonded pairs of gaseous water molecules – in conditions similar to Earth's atmosphere. Such dimers have been predicted to have important effects on the Earth's radiation balance and atmospheric chemistry, so this latest breakthrough could help scientists gain a better understanding of how their presence affects climate.

Water dimers could abound in the atmosphere

Water vapour is the third most common gas in the Earth's atmosphere, and the principal absorber of both sunlight and the Earth's blackbody radiation. Scientists have known for decades that water appears to absorb more radiation than theoretical models suggest that it should. In the

1960s the Russian astronomer Sergei Zhevakin suggested that this discrepancy could be explained if, among the free water molecules (monomers), hydrogen bonding caused a small proportion of water molecules to pair-up to create dimers. These dimers, suggested Zhevakin and others, would be much stronger absorbers than single water molecules.

While chemists have been able to study water dimers at temperatures near absolute zero, it was not clear whether the structures could even form under conditions found in the Earth's atmosphere. This is because the infrared spectral signatures of a dimer are extremely difficult to separate from those of single water molecules – making standard spectroscopy techniques unable to answer the question.

Promising rotational spectra

Much more promising are the rotational spectra of dimers and monomers, which calculations suggest should be much more distinct than infrared spectra. These features appear in the extremely high-frequency (EHF) region of the radio spectrum – at about 100–200 GHz – and should differ significantly because dimers have much higher moments of inertia than monomers. Unfortunately, standard spectrometers did not have sufficient resolution to detect these faint, broad peaks predicted by quantum-chemistry calculations.

Now, using a special spectrometer, researchers at the Russian Academy of Sciences in Nizhgy Novgorod led by Mikhail Tretyakov – a former student of Zhevakin – have made the first clear observations of water dimers under conditions similar to those in the atmosphere. The team created a new spectrometer in which EHF radiation is injected into a cavity with a mirror at either end. The resonance of the cavity depends on the separation between the mirrors, which is controlled extremely precisely. Gas is then injected into the cavity and the frequency is varied. At frequencies the gas does not absorb, the cavity shows one sharp peak at its expected resonant frequency. However, at frequencies near the absorption peaks of the gas, the resonance peak becomes broader. By measuring this change in the sharpness of the peak, the researchers were able to measure resonances associated with water dimers.

The researchers injected water vapour into the cavity at a similar temperature (23 °C) and partial pressure to that found in the atmosphere. Previous attempts to detect the water dimer at ambient conditions have focused on a single peak, which is difficult to assign unambiguously to a particular molecule. Instead, the researchers identified a distinct series of four peaks in the absorption spectrum. These occurred at exactly the same positions as measured in cold-temperature experiments. The researchers interpret this as clear evidence that water dimers can form in water vapour under ambient conditions.

Puzzling peaks

There is one puzzling aspect of the results, however: the measured absorption peaks were four times broader than those predicted by computer modelling. The researchers speculate that the reason may lie in the simplifying assumptions about the structure of the water molecule that are made by the computer model. For example, the water molecule is assumed to be symmetric, whereas in reality this is not quite true.

David Wales, a theoretical chemist at the University of Cambridge, said that while a full explanation of the broadness of the lines is important, the identification of four peaks makes the detection of the dimer quite convincing anyway. "It will inspire a lot of new work, both theoretical and experimental," he said.

Tretyakov agreed that more work needs to be done: "First of all, I need to improve the signal-to-noise ratio of the spectrum – I know how to do that now. After that, I can get more information on the quantitative properties of the water dimer, and this will help us to understand the properties of liquid water in the long run."

The research is published in **Physical Review Letters**.

About the author

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