

with estimates from various temperature proxies, says Zeke Hausfather of C3 Energy in Redwood City, California. In future work, the Berkeley team plans to incorporate marine temperatures, as the other three groups have done, since oceans represent 70% of Earth's surface.

Thomas Karl, NCDC director, welcomes the entry of a fourth independent research group that makes different assumptions to analyze the same variable. Gavin Schmidt of NASA's GISS comments that the particular approach taken by the Berkeley team addresses several specific criticisms: that the prior analyses did not use enough data and that they used flawed procedures for correcting data discontinuities.

Differing approaches

A key distinction of the Berkeley group's treatment is that it allows analysts to handle short and discontinuous temperature records; the other three groups, by contrast, have relied on stations with fairly long temporal records, usually on the order of decades. No more than about 8000 sites have been included in past analyses. The Berkeley group works with temperature records from about 40 000 sites.

One of the first steps in calculating a global temperature is to homogenize the data—that is, detect and correct for discontinuities in the temporal data set from each station. For example, analysts may compare the time records

from adjacent stations, which should be experiencing roughly the same weather conditions. Any jump in one time series not seen in others is flagged, and the dataset is adjusted accordingly.

When the Berkeley collaborators encounter a discontinuity, they break the data set into two records and treat the resulting fragments as independent records from the same location. Such an approach effectively multiplies the number of record fragments they handle by about a factor of four, to something like 170 000. The compensation for the discontinuities—or offsets—is determined by the team's global statistical treatment.

For any global temperature esti-

Water dimer yields to spectroscopic study

Water is Earth's principal greenhouse molecule: It's responsible for well over half of the atmosphere's absorption of solar and terrestrial radiation. So it's a crucial ingredient in any model of Earth's radiation balance and climate. But the study of atmospheric water's absorption spectrum has for decades

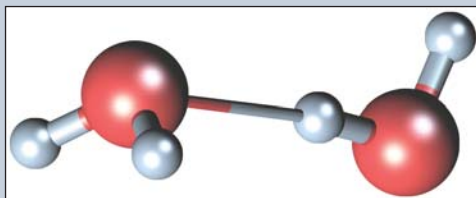
been fraught with mystery and controversy. In addition to the expected spectral lines—corresponding to transitions between discrete rotational, vibrational, and electronic quantum states—the spectrum includes a broad continuum absorption that has yet to be fully explained.¹

Beginning in the late 1960s, and especially since the late 1990s, some researchers have suspected that at least part of the continuum could be due to water dimers. As gas-phase molecules collide with one another, every so often two of them form a hydrogen bond (as shown in the figure), remain together for a time, and then go their separate ways. The dimer would have a different set of quantum states than the monomer and thus a different spectrum.

But dimers had never been spectrally characterized at ambient temperatures, so no one knew whether the dimer absorption actually matched the water absorption features they sought to explain. The dimer spectrum was also needed for measuring the dimer's prevalence under atmospheric conditions—or for confirming that it was present in appreciable quantities at all.

Through the years many groups have tried to measure the dimer's vibrational spectrum in the IR. Two high-profile papers claimed detection, but both failed to stand up to scrutiny.² The problem was that dimers could be formed only in the presence of many more water monomers, and the vibrational modes of the weakly bound dimer were just too difficult to convincingly disentangle from those of the monomer.

The rotational spectrum was in many ways more promising. The dimer and monomer have completely different moments of inertia, so their rotational spectra should not overlap as much. And rotational spectra comprise many equally spaced spectral lines, which can be more conclusively identified than isolated vibrational lines. But rotational transitions occur at microwave frequencies, and traditional microwave spectrometers lack the sensitivity to detect the weak dimer spectrum.



Mikhail Tretyakov and colleagues at the Institute of Applied Physics of the Russian Academy of Sciences in Nizhny Novgorod have remedied that problem by building a microwave resonator spectrometer based on a Fabry–Perot cavity. An absorbing sample placed in the cavity reduces the

cavity's *Q* factor. By measuring changes in the *Q* factor, the researchers can record microwave spectra with unprecedented sensitivity.

In collaboration with theorist Claude Leforestier (University of Montpellier, France), who had computationally predicted the dimer's rotational spectrum, Tretyakov and colleagues realized that their spectrometer might be able to detect dimers in room-temperature water vapor at low pressure.³ It took them three years to upgrade their instrument to make the low-pressure measurements. But as soon as they did, they saw four equally spaced absorption peaks exactly where Leforestier said they would be.⁴

The observed peaks are four times broader than predicted, and they barely rise above the noise. Tretyakov and colleagues attribute the difference to a simplifying approximation made in the calculations: that the dimer is a symmetric rotor with two equal moments of inertia. Accounting for the dimer's slight asymmetry, and for its many low-frequency vibrational modes that influence the rotational spectrum, would have made the calculations prohibitively difficult. Still, it came as a surprise that the approximation would affect the width of the peaks but not their placement.

The next step for the researchers is to measure the spectrum under different temperatures and pressures and at different wavelengths—information that they need before they can begin to investigate the dimer's involvement in the atmosphere. They also hope to use their spectrometer to detect even more elusive atmospheric species, such as a water–nitrogen complex.

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References

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