

Study documents reaction rates for three chemicals with high global warming potential

January 26 2010



Georgia Tech researchers work in their laboratory with equipment used to study reaction rates of three key greenhouse gases. Shown are Patrick Laine, J. Michael Nicovich, Paul Wine and Zhijun Zhao. Credit: Georgia Tech Photo: Gary Meek

A study published this week in the journal *Proceedings of the National Academy of Sciences (PNAS)* provides new information about the rates at which three of the most powerful greenhouse gases are destroyed by a chemical reaction that takes place in the upper atmosphere.

The three compounds are potentially important because they absorb infrared energy in the so-called "atmospheric window" region - at wavelengths where other major greenhouse gases such as carbon dioxide allow radiation to pass freely out into space. Though these long-lived compounds now exist in relatively low concentrations, their ability to

absorb energy at these wavelengths means their contributions to [global warming](#) could increase if their levels continue to rise.

Because the compounds are relatively inert chemically, information on how they react with electronically excited atomic oxygen - known as O(1D) - will help improve the accuracy of global climate models by providing a better estimate of how long these absorbers remain in the atmosphere. The information could also inform public policy debate about whether the chemicals, now used in industrial applications, should be replaced with compounds that have less climate change impact.

"This study will contribute to an understanding of the long-term effect of these compounds on climate," said Paul Wine, a professor in the Schools of Chemistry and Biochemistry and Earth and Atmospheric Sciences at the Georgia Institute of Technology. "There is significant interest in trying to establish the role of these heavy absorbers of [infrared radiation](#), especially the compounds that absorb in the window region where other greenhouses gases are not factors."

Information on the reaction rates of sulfuryl fluoride (SO_2F_2), nitrogen trifluoride (NF_3) and trifluoromethyl sulfur pentafluoride (SF_5CF_3) was published Jan. 25, 2010, in the early edition of the *PNAS*, and will be part of a special issue on [atmospheric chemistry](#). The research was funded by the National Aeronautics and Space Administration (NASA).

Sulfuryl fluoride is a fumigant widely used as a replacement for the ozone-depleting compound methyl bromide (CH_3Br). Nitrogen trifluoride is used in the electronics industry for plasma etching and equipment cleaning. Trifluoromethyl sulfur pentafluoride - the most powerful known [greenhouse gas](#) on a per-molecule basis - is believed to be a breakdown product of an insulating compound used in high-voltage equipment.

The three compounds have some of the highest global warming potentials (GWP) of any compounds in the atmosphere. Trifluoromethyl sulfur pentafluoride has a global warming potential approximately 18,000 times greater - on a per unit mass basis - than carbon dioxide when evaluated over a 100-year time period. Nitrogen trifluoride has a GWP of approximately 17,000, while sulfuryl fluoride is approximately 4,000 times more effective than carbon dioxide at trapping infrared radiation.

The presence of these compounds in the atmosphere and their potential contributions to climate change were only recently recognized. Reaction with electronically-excited oxygen atoms is the only known pathway by which these compounds are destroyed at atmospheric altitudes below the ionosphere. Though present at relatively low levels today, studies show that their concentrations are increasing - with atmospheric levels of NF_3 growing at more than 10 percent per year.

"These chemicals are relatively inert, which makes them useful for specific applications," Wine said. "But because of their chemical inertness, they tend to have long lifetimes in the atmosphere and are available to trap radiation for a long time. That contributes to their high global warming potential."

To study the rate at which the compounds react with and deactivate the atomic oxygen species, Wine and Georgia Tech collaborators Zhijun Zhao, Patrick Laine and J. Michael Nicovich used laser flash photolysis in the laboratory to create $\text{O}(1\text{D})$ and expose it to the three compounds in controlled environments at temperatures ranging from about 200 to 350 degrees Kelvin.

$\text{O}(1\text{D})$ is produced in the atmosphere by the interaction of ozone (O_3) and molecular oxygen (O_2) with ultraviolet light. This electronically-excited oxygen interacts quickly with other molecules around it - such as

N_2 and O_2 - to form ground-state [atomic oxygen](#). Hence, its levels are higher in the upper atmosphere than in the lower atmosphere.

The researchers found that O(1D) interaction with trifluoromethyl sulfur pentafluoride destroys this compound in - at most - one out of a thousand interactions. That means amounts of that compound released into the atmosphere will remain there for long periods of time, probably around a thousand years.

For NF_3 , the researchers found a reaction rate more than double one that had been reported in a previous study, meaning the material may have less warming impact than previously thought. For SO_2F_2 , which also may be taken up by the ocean, the Georgia Tech findings agreed with one earlier study.

Wine said the new data on these compounds will be factored into the next major report of the Intergovernmental Panel on Climate Change. Knowing how long the compounds will likely remain in the atmosphere permits more accurate accounting for what could be a significant infrared trapping effect.

"If you put new molecules into the atmosphere that absorb infrared radiation where CO_2 and methane already absorb, they would have to be present in very large quantities to have any effect at all," Wine noted. "But because these molecules absorb in the window region at wavelengths between 8 and 12 microns, they don't have to be present at high levels to have an effect."

Provided by Georgia Institute of Technology

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