Stratospheric Ozone: How We Came to Understand its Chemistry and Response to Perturbations

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A few background facts

- Ozone in atmosphere “discovered” by measurement of cutoff of solar spectrum in UV (Cornú 1879, Hartley 1881)

- Ozone determined to be a layer at high altitude (in stratosphere) (Strutt [Rayleigh] 1917)

- Ozone column amount quantitatively measured by UV absorption (Fabry and Buisson 1919, Dobson 1924)

- First ozone theory by Chapman (1930)
Historical Context

• The ozone issue was first posited in terms of Supersonic Transports (SSTs) impacting the atmosphere by Harold Johnston in 1971.
• The “fluorocarbon-ozone” theory was put forward by Molina and Rowland in 1974
• The negotiations for the Montreal Protocol were begun in 1985 and formulated into the protocol by 1987
• The ozone hole was discovered in 1985 and explained reasonably well in 1986
• Measurements showing anti-correlation of chlorine and ozone in the Antarctic vortex were made in 1987

• How was so much discovered and explained in such a short time (16 years)?
Some Chemistry History

Early work: study of ozone photochemistry in the laboratory

Fritz Weigert (1907) noted that addition of Chlorine (Cl₂) sped up rate of ozone recombination – work was contemporary with early work on photosynthesis and on the photoelectric effect

Sydney Chapman proposed the first ozone theory for the stratosphere in 1930

Norrish and Porter – Nobel prize in chemistry 1967 for techniques to detect small concentrations of short-lived radicals

Paul Crutzen, in 1970, developed the early theory of the catalytic impact of nitrogen and hydrogen oxides on stratospheric ozone

Harold Johnston, in 1971, suggested that nitrogen oxides from proposed SSTs could deplete stratospheric ozone – CIAP program followed

Molina and Rowland proposed that stratospheric ozone could be destroyed by chlorine released in the stratosphere from CFCs in 1974

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H. J. Schumacher and the Ozone Chemical Mechanism


Before: excited ozone molecules

After: oxygen atoms from photodissociation

netics of the reaction. If we assume for the primary reaction the formation of an excited ozone molecule

\[ \text{O}_3 + h\nu \rightarrow \text{O}_3' \]  

(1)

we have only a limited number of possible reactions that may follow, namely

\[ \text{O}_3' + \text{O}_3 \rightarrow 2\text{O}_2 \]  

(2)

\[ \text{O}_3' + \text{O}_2 \rightarrow \text{O}_2 + \text{O} \]  

(3)

\[ \text{O}_3' + \text{O}_2 \rightarrow \text{O}_3 + \text{O} \]  

(4)

These considerations show that the reaction

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} \]

is quite probable. Neglecting the formation of chains, only the following reactions are possible

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O} \]  

(1)

\[ \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \]  

(2)

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]  

(3)
Ozone Photochemistry
Odd Oxygen (O atoms + O₃ molecules)

Chapman Theory 1930

Initiation: \( h\nu + O_2 \rightarrow O + O \)
(\( \lambda < 240 \text{ nm} \))

Propagation: \( O + O_2 + M \rightarrow O_3 + M \)
\( h\nu + O_3 \rightarrow O_2 + O \)
(\( 200 \text{ nm} < \lambda < 300 \text{ nm} \))

Termination: \( O + O_3 \rightarrow O_2 + O_2 \)

Ozone is continuously being made and destroyed in the atmosphere
Catalysis Accelerates Termination Reaction

Hydrogen oxides, Nitrogen oxides
Chlorine oxides, Bromine oxides

Example: Chlorine

\[
\begin{align*}
\text{Cl} + \text{O}_3 & \rightarrow \text{ClO} + \text{O}_2 \\
\text{ClO} + \text{O} & \rightarrow \text{Cl} + \text{O}_2 \\
\text{O} + \text{O}_3 & \rightarrow \text{O}_2 + \text{O}_2 \quad \text{net}
\end{align*}
\]

Fritz Weigert first studied the impact of chlorine on ozone decomposition in his laboratory in 1907.
The Nobel Prize in Chemistry 1967
Manfred Eigen, Ronald G.W. Norrish, George Porter

The Nobel Prize in Chemistry 1967 was divided, one half awarded to Manfred Eigen, the other half jointly to Ronald George Wreyford Norrish and George Porter "for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy".
Early Synthesis of CFCs

Frederic Swarts

Belgian chemist: (1866 -1940). Swarts was one of only about a half dozen fluorine chemists in the world in the late part of the 19th century; he prepared the first chlorofluorocarbon, CFC-11 in the early 1890s.

\[ \text{SbF}_3\text{Br}_2 + \text{CCl}_4 \rightarrow \text{CFCl}_3 \text{ (CFC-11)} + \text{SbF}_2\text{Br}_2\text{Cl} \]

CCl₄ synthesized in 1839 by Regnault

Thomas Midgley, Jr

1930: GM charged Midgley with developing a non-toxic and safe refrigerant for household appliances. He (along with Charles Kettering) synthesized dichlorodifluoromethane (CHCl₂F). CFCs replaced sulfur dioxide, methyl chloride or ammonia gases (toxic or explosive substances) previously used in heat pumps and refrigerators.

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The Curious Case of Thomas Midgley

- Came up with CFCs as a replacement for dangerous chemical in refrigerators, e.g. ammonia, sulfur dioxide

- Midgley also synthesized tetraethyl lead to reduce knocking in auto engines

Midgley became ill with polio and invented a mechanical bed to assist him: but he died of his own invention when he became entangled in the pulleys and strangled himself!
Stratospheric Meteorology, Dynamics, and Ozone

Léon Teisserenc de Bort discovers the stratosphere – a layer in which temperature no longer decreases with altitude.

Brewer-Dobson Circulation (1951) helps explain water vapor and ozone distributions in the stratosphere.

Unique nature of Antarctic vortex is revealed during the IGY 1957-8.

Dobson summarizes (1966) ozone measurements of IGY showing clear difference between Antarctic and Arctic.

Polar Stratospheric Clouds are shown to be a ubiquitous feature of the winter Antarctic stratosphere.

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How did we get involved personally in chlorine chemistry in the atmosphere?

Stedman, circa 1972: “Chlorine destroys ozone; everybody knows that!”
How did we come to know about the importance of CFCs?

Article


**Stratospheric sink for chlorofluoromethanes: chlorine atomc-atyalysed destruction of ozone**

Mario J. Molina & F. S. Rowland

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Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the Chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.
The information was out there for people like us to have put forward the fluorocarbon-ozone theory – but we didn’t!


Chuck Kolb (to me), November 1973

“Have you ever thought about Freons? They are inert in the troposphere, not soluble and don’t absorb visible light. They will get up into the stratosphere where uv will produce chlorine.”

Jim Walker

“What about Carbon tet?”

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Rowland heard a talk by Lovelock – his notes below were the basis for studies by his new post-doc, Mario Molina
Ozone Hole Discovery

Discovered at the British Antarctic Survey station at Halley Bay from measurements begun during the IGY

Farman, Gardiner, & Shanklin (1985)

Satellite measurements showed that Halley Bay was in best location for seeing ozone hole

Original TOMS ozone hole map produced by Don Heath and PK Bhartia in 1985

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Figures from our 1986 Nature paper on the ozone hole

Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease


NASA/Goddard Space Flight Center, Laboratory for Atmospheres, Greenbelt, Maryland 20771, USA

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What about the theory of the ozone hole?

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Variety of Initial Theories of the Ozone Hole

- Chlorine chemistry

- Dynamics – was ozone just moved around by wave motions but conserved over the entire polar region? No, there was a net decrease.

- Solar Cycle – $\text{NO}_x$ chemistry variations induced by solar cycle- required $\text{N}_2\text{O}$ change that was not observed.

- Other?
Feldafing Workshop, June 1984

The rationale for the scope of the present assessment report was based on information gained at a scientific workshop, entitled "Current Issues in Our Understanding of the Stratosphere and the Future of the Ozone Layer" which was held in Feldafing, Federal Republic of Germany in June 1984 with international participation, co-sponsored by NASA, FAA, WMO, and BMFT.

Sherry Rowland: “Missing Chemistry”

– Don’t need to worry about fast channels
– What if one reservoir molecule reacted with another, e.g. ClONO₂ and HCl?
– Molina (and Sato and Rowland independently) had been studying this reaction in the lab
– They found a small, but measureable rate coefficient
– Inserted into a model, the reaction implied that 30% of the global amount of ozone should have already disappeared
– Later reported that reaction was occurring on teflon walls of the experiment
Chlorine Photochemistry (normal)

- Active Chlorine < 0.5%
- Chlorine Reservoirs
Polar Stratospheric Clouds (PSCs)

**Fig. 1.** Saturation mixing ratios of water vapor with respect to ice (in ppm, i.e. units of \(10^{-6} \text{ g H}_2\text{O/g air}\)) vs pressure for Maudheim base \((70^\circ 03' S, 10^\circ 56' W)\) during the 1950 Antarctic winter. The curves extend up to the bursting level of the balloons. The temperature data used were half-monthly means. The position of the half-monthly mean tropopause is indicated. The approximate dates over which “Stratospheric Cist” were reported are also indicated.

*Tellus (1977), 29, 531–534*

**On the nature of persistent stratospheric clouds in the Antarctic**

By JOHN L. STANFORD, Physics Department, Iowa State University, Ames, Iowa 50011, U.S.A.

(Manuscript received November 8, 1976; in final form January 26, 1977)

**ABSTRACT**

This persistent very high clouds called “Stratospheric Cist” were reported at Maudheim base \((70^\circ 03' S, 10^\circ 56' W)\) during the 1950–51 austral winters. The nature of these clouds, whether they are \(\text{H}_2\text{O}\) or dust, is of importance in the proposed sink for stratospheric moisture in the Antarctic winter.

Results are presented from analyses of unpublished daily cloud reports and daily upper air measurements from the Maudheim expedition. The results reveal strong evidence that the “Stratospheric Cist” were stratospheric ice clouds. Given this identification, an upper limit of 6–7 ppm can be assigned to the water vapor mixing ratio in the lower stratosphere for the 1950–51 Antarctic winters.

*Journal of Geophysical Research, Vol. 87, No. C7, Pages 5001–5008, June 20, 1982*

**A Model of the Antarctic Sink for Stratospheric Water Vapor**

**Anne R. Douglass** and **John L. Stanford**

Department of Physics, Iowa State University, Ames, Iowa 50011

Model calculations have been performed to quantitatively estimate the amount of stratospheric \(\text{H}_2\text{O}\) removed by freeze out during the winter in the Antarctic region. The model uses realistic temperature and wind fields based on Hartmann’s Nimbus 5 temperature grids. For the 1993 Antarctic winter stratosphere, initial water vapor mixing ratios of 2.7 and 3.0 ppm lead to removal of 1.6 and 2.7 \(\times 10^{16}\) kg \(\text{H}_2\text{O}\) from the lower stratosphere. This annual sink magnitude is small, representing about 0% of the total stratospheric \(\text{H}_2\text{O}\) burden and about 10% of the apparent sink identified by Ellingson (1974). However, a sink of this magnitude is close to the lower rate estimates of water produced in the stratosphere by methane oxidation. The sink is not large enough to balance additional, proposed water vapor sources.
Chlorine Photochemistry (polar)

Active Chlorine Increases By 50 to 100x

PSC Reactions Drain Chlorine Reservoirs

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This still did not make ozone go away fast enough to explain the ozone hole


**Production of Cl₂O₂ from the Self-Reaction of the ClO Radical**

L. T. Molina and M. J. Molina*

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(Received: April 22, 1986; In Final Form: September 15, 1986)

- \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \) (x2)
- \( \text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2 \)

net: \( 2\text{O}_3 \rightarrow 3\text{O}_2 \)

without involvement of atomic oxygen
“Smoking Gun Slide”
Quickly demonstrated that the chlorine theory of the ozone hole was the correct theory
What is significant about the Montreal protocol?

- “Living” protocol: provision for updates
- Fund for developing countries to offset cost of potentially more expensive alternatives
- Participation of scientists, government officials, industry, and environmental organizations
- Based on scientific assessments from 3 panels
  - Scientific Assessment Panel (SAP)
  - Environmental Effects Assessment Panel (EEAP)
  - Technology and Economic Assessment Panel (TEAP)

Richard Benedick was the chief US negotiator for the Protocol.
The Montreal Protocol

History

- March, 1985: Vienna Convention for Protection of the Ozone Layer
- Sept 16, 1987: opened for signature
- Jan 1, 1989: entered into force
- May, 1989: first meeting of the parties

Revisions or Amendments

- 1990 London
- 1992 Copenhagen
- 1997 Montreal
- 1999 Beijing
- 2007 Montreal
International Ozone Assessments

WMO World Plan of Action on the Ozone Layer - 1977

WMO The Stratosphere 1981: Theory and Measurements

WMO Atmospheric Ozone - 1985

Other NASA and Climatic Impact Assessment Program (CIAP) reports prior to 1981 were primarily performed in the USA


Safeguarding the Ozone Layer and the Global Climate System: 2005 (IPCC/TEAP)

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An aside on giving talks on hot issues such as the fluorocarbon-ozone issue was at one time

- You are an expert on science: separate your science from any opinions on what should be done by society.

- There are no dumb questions: Even if you have heard a question a thousand times, respect the questioner.

- Be prepared: you know the standard questions so you should have a prepared approach to these.

- If you don’t know the answer, say so.
Comments on the Future of Stratospheric Ozone

• Chlorine is being removed from the atmosphere as the Montreal Protocol limits CFC and HCFC production

• Ozone should recover, but not to the same levels because of the changes in greenhouse gases that also impact ozone

• Future amounts of ozone will be controlled by nitrous oxide ($N_2O$) and carbon dioxide ($CO_2$)
We put these together into an “Equivalent Effective Stratospheric Chlorine” or EESC
The Post-CFC Ozone Layer
What will the stratospheric ozone layer look like after CFCs have been removed?

- Greenhouse gases cool the stratosphere
- Cooling slows ozone loss in upper stratosphere leading to ozone increase
- Lower stratospheric circulation speeds up leading to tropical ozone decrease and mid-latitude ozone increase

Results from the GEOS CCM 2065-1980

Net result is a column ozone increase at mid to high latitudes and almost no change near the equator

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What about $\text{N}_2\text{O}$?

- $\text{N}_2\text{O}$ is the source of $\text{NO}_y$ that can catalytically destroy ozone
- Several papers have claimed that increasing $\text{N}_2\text{O}$ is an existential threat to the ozone layer
- The situation is a bit more complex
N atoms, formed by photolysis of NO, can either reform NO or can react with NO to remove NO$_y$

\[ \text{N} \xrightarrow{h\nu} \text{NO} \xrightarrow{O_2} \text{N}_2 \]

\[ K_{N+O_2} = 1.5 \times 10^{-11} \exp(-3600/T) \]

The branching ratio is strongly temperature dependent: low temperatures $\rightarrow$ more NO$_y$ loss
The evolution of stratospheric NO$_y$

- Depends on the relative change of N$_2$O and CO$_2$ in the future
- A1b scenario leads to constant future NO$_y$
- A2 scenario leads to increasing NO$_y$

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Ozone Scenarios

- Chlorine dominates ozone change
- Amount of global “super-recovery” depends on relative scenario for $\mathrm{N}_2\mathrm{O}$ and $\mathrm{CO}_2$ change
Final thoughts

- Details are important, but if you don’t try to step back and see the big picture you can waste a lot of time on the wrong details.
- Opportunities abound: will you recognize them? Will you follow up on them? Or will you just let them pass by?
- Ideas are cheap – Selection of good ones and follow through on them is what counts.