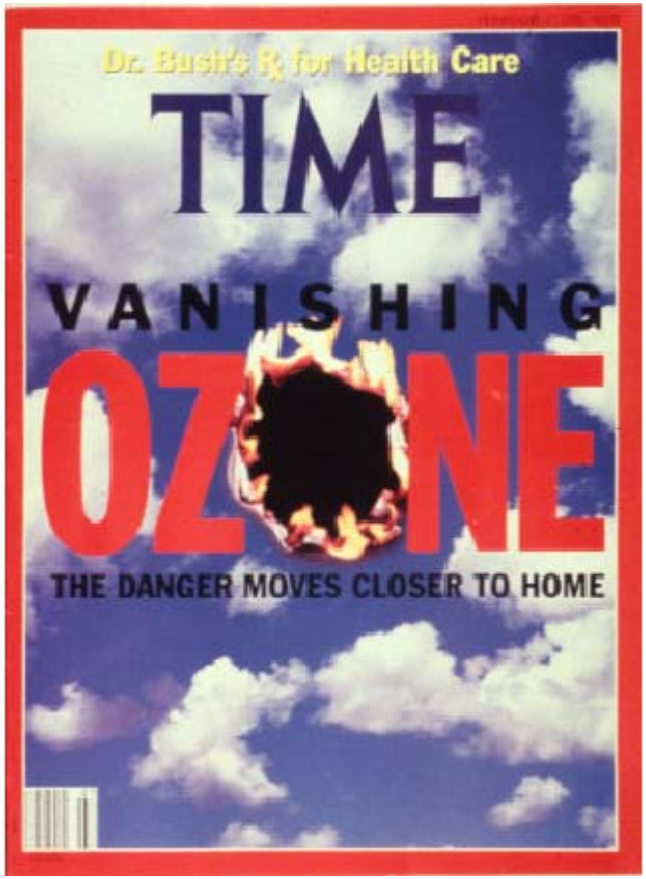
Clouds are the Earth's Blanket

The Chemistry of Stratospheric Ozone Depletion

- Chemistry and Photochemistry in the Stratosphere
- The Antarctic Ozone Hole
- Molecular Beam/Laser Spectroscopic Studies of Photochemistry

Ozone in the News



➪ Nations meet in Montreal to discuss global agreement on banning CFC chemicals, not usually done except for chemical warfare ageints.

➪ CFC's are in everyone's home already, so they're not killing anyone right now.

➪ Rush Limbaugh says it's a fraud, a scientific consipracy, grant grubbing, and government just interfering with our lives.

➪ What's going on?

➪ An otherwise arcane area of chemistry catapulted into international prominence. A combination of lab measurements, satellite data, plane flights, and physical chemistry is needed to piece the puzzle together of why ozone is being lost.

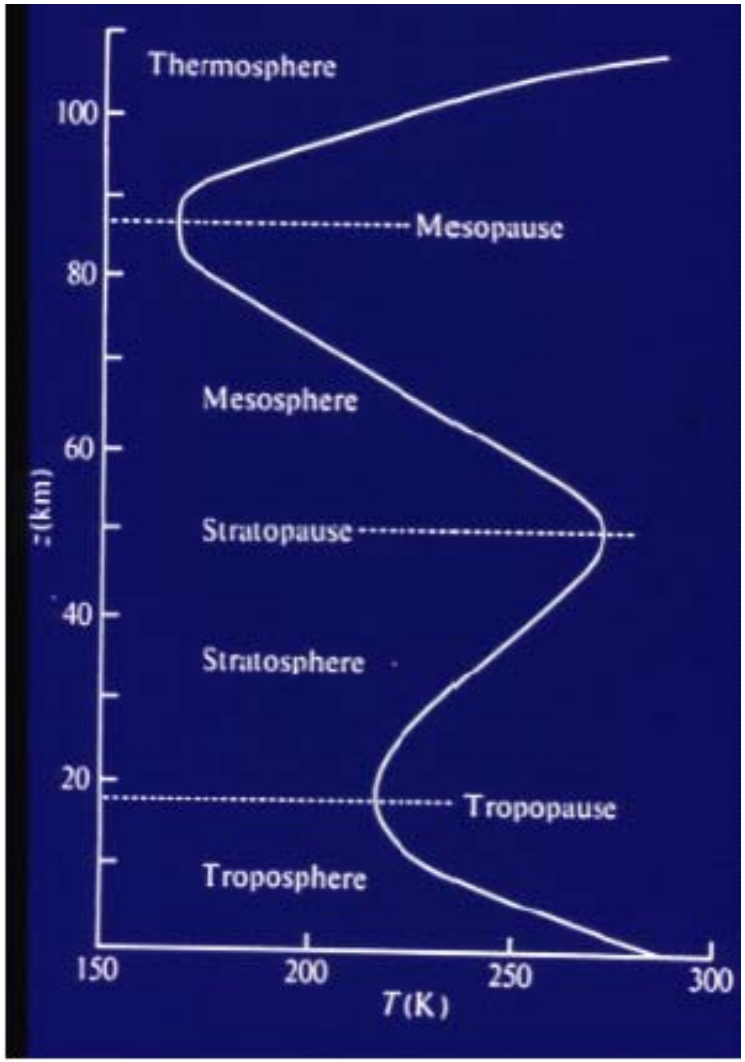
A Problem with No National Boundaries

Air Conditioner Repair Man
Arizona says CFC's are OK
CFC's smuggled in from Mexico, which also OK's CFC's

The Ozone Shield

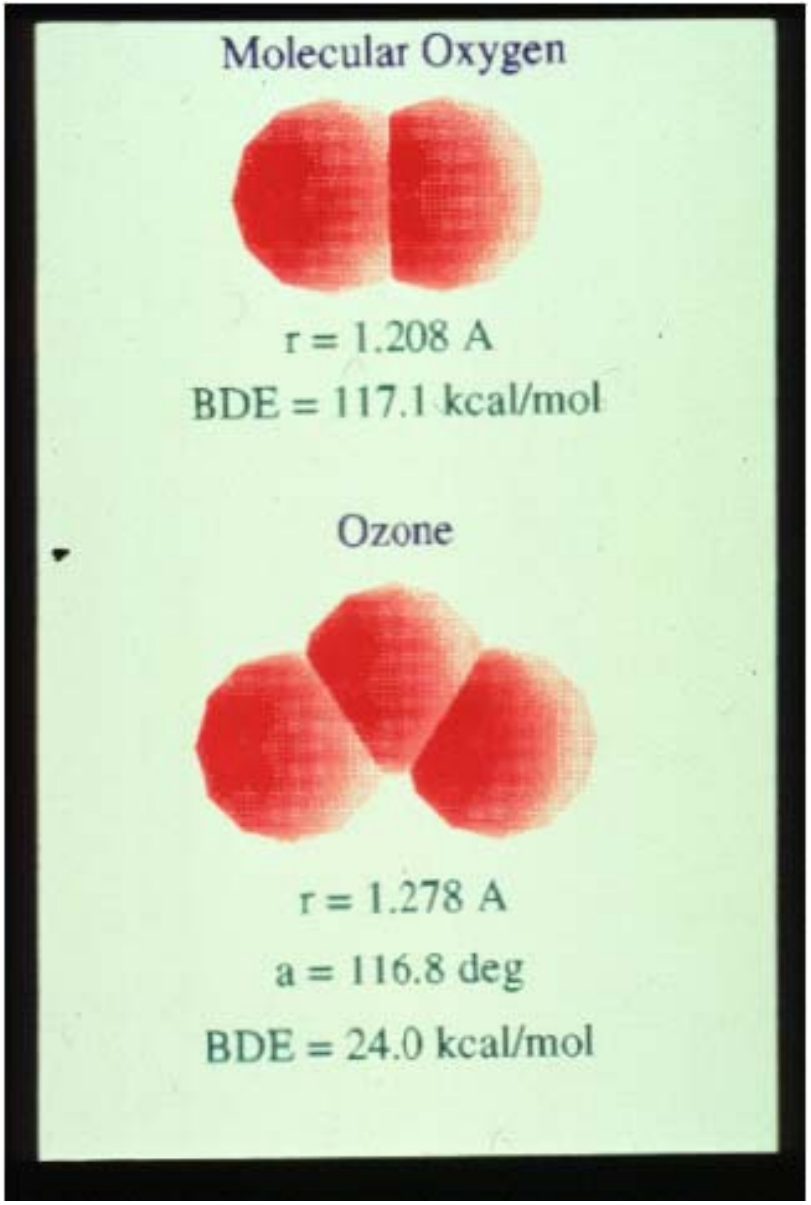
Less than 0.5% of Earth's Radius;
Protects all life on earth

Temperature Profile in the Atmosphere

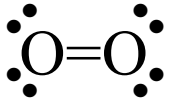


Stratosphere
T *increases* with increasing altitude;
Due to absorption of sunlight by ozone
From 15-60 km

Troposphere
T decreases with increasing altitude;
Adiabatic cooling as density gets lower
Minimum defines tropopause

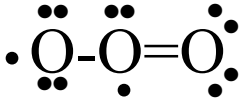


O_2 , Dioxygen
Octet on each atom
Stable



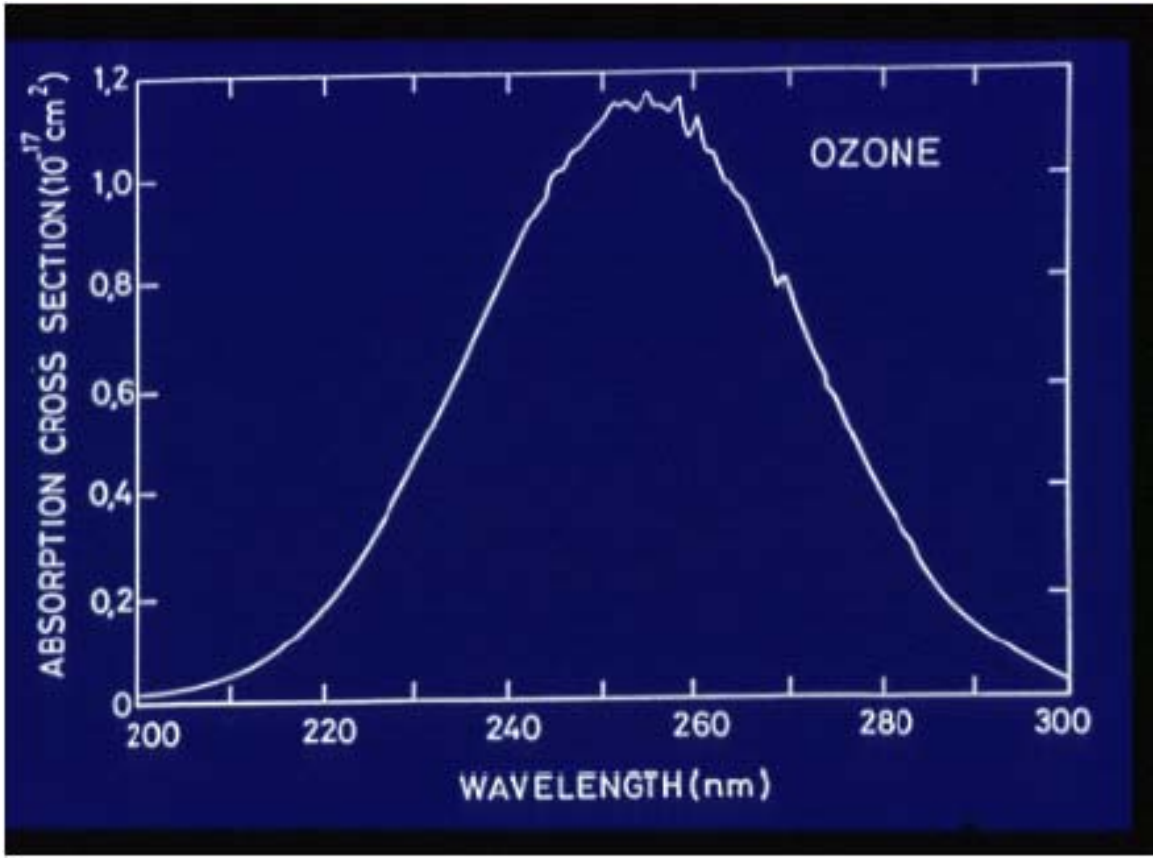
21% of atmosphere

Ozone, O_3
Non-octet



4 times weaker bond
Reactive and caustic

Ozone Absorption Spectrum

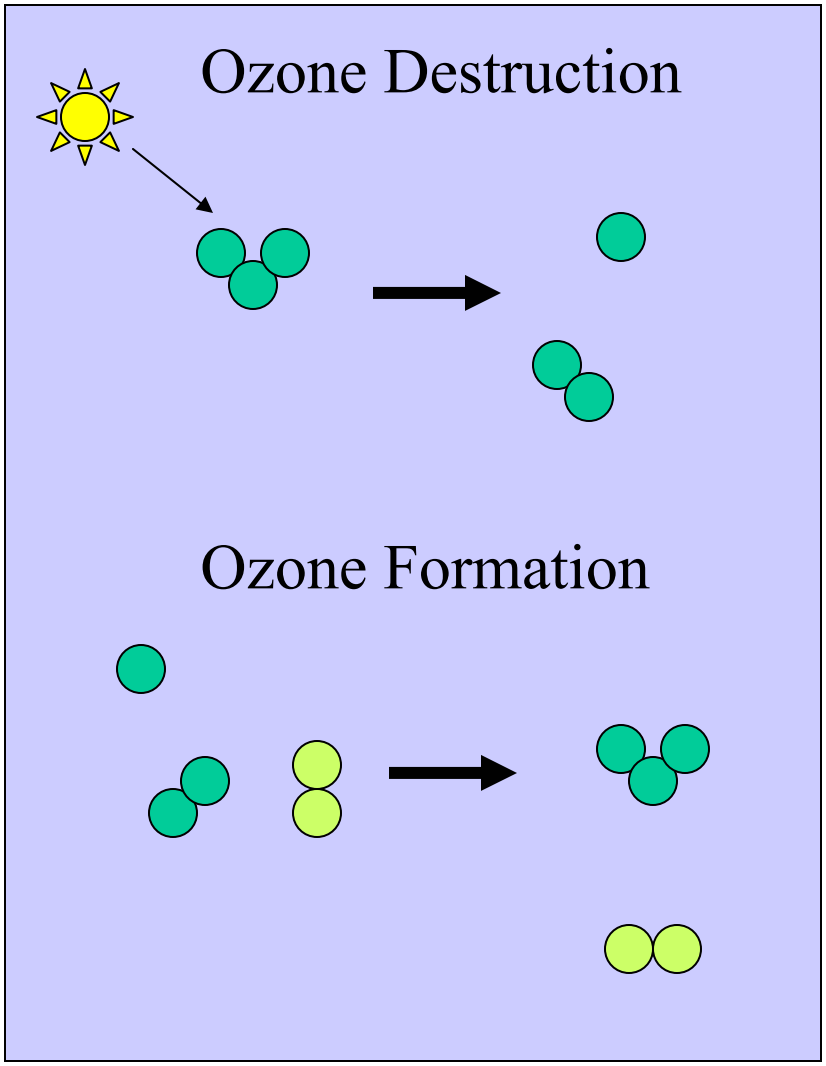


Absorbs light between 220 and 300 nm

N_2 and O_2 do not absorb at those wavelengths

Protects DNA from UV light and damage

Chapman Cycle: 1930's

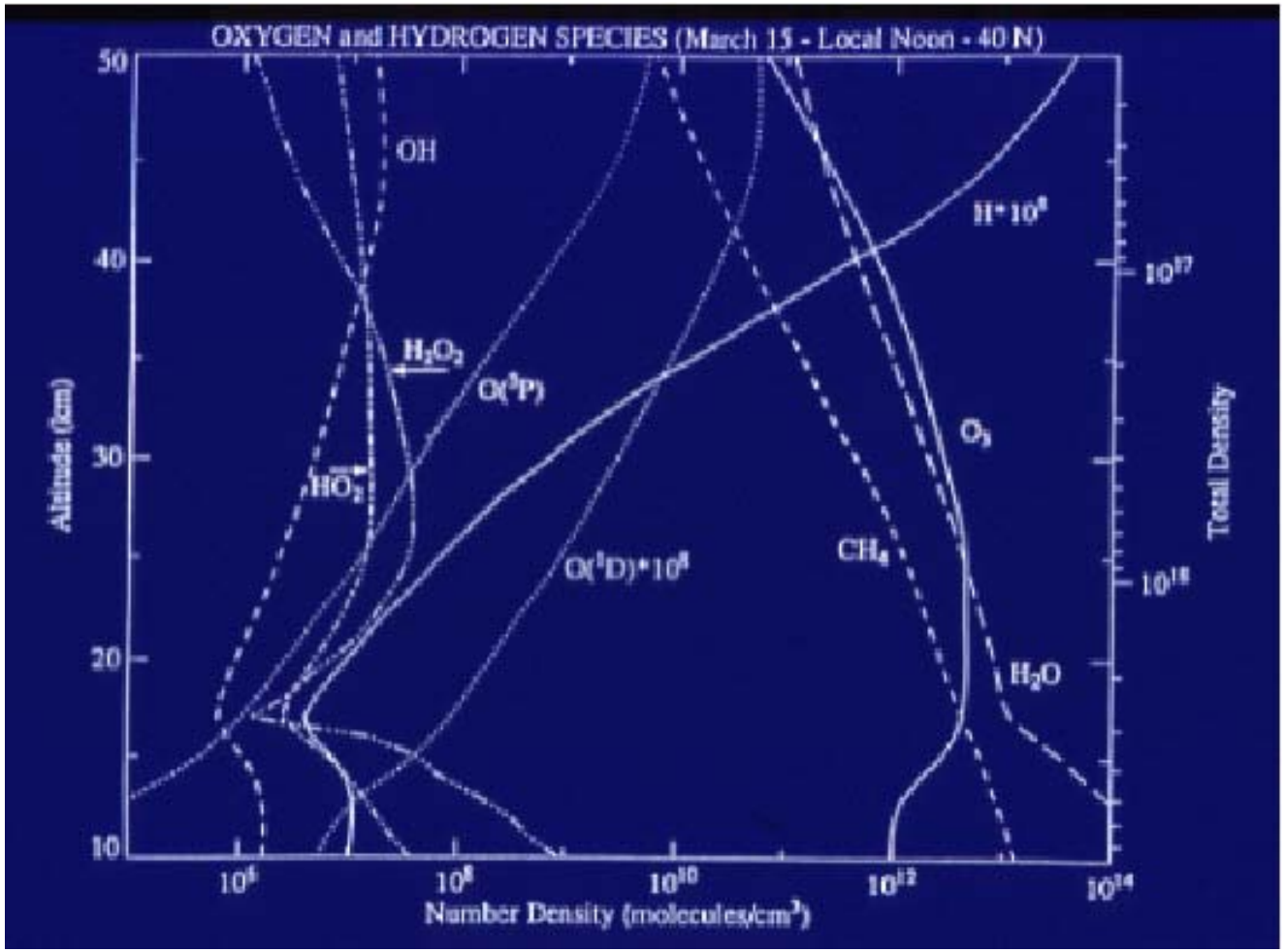


Light absorption breaks the O-O bond in ozone
Forms O•

In presence of a third body, forms O_3 again

Does NOT explain ozone hole

Concentration of Species in the Atmosphere



Water and Ozone are highest, by far
Others are small, but they don't have 8 electrons!

Little Things Mean a Lot

Total Pressure:	20-200 Torr
H_2O	1-10 ppm
O_3	1-10 ppm
ClO	0.1-3 ppb
BrO	1 ppt
O	1 ppt-1ppb
Cl	0.1 ppt-10 ppt

Free Radicals

Molecule with odd number of electrons
"Open Shell"
Typically highly reactive

Some atmospheric radicals

Cl, Br	H	O
ClO	OH	NO
BrO	O_2H	

Radical Chain Reactions

Initiation

$$Cl_2 + h\nu \longrightarrow Cl\cdot + Cl\cdot$$

Propagation (by each Cl atom)

$$Cl\cdot + CH_4 \longrightarrow HCl + \cdot CH_3$$

$$\cdot CH_3 + Cl_2 \longrightarrow CH_3Cl + Cl\cdot$$

Etc., etc…..until

Termination (example)

$$Cl\cdot + \cdot Cl \longrightarrow Cl_2$$

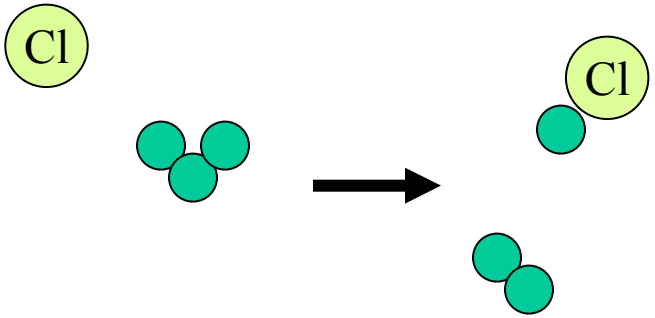
or

$$Cl\cdot + \cdot CH_3 \longrightarrow CH_3Cl$$

One photon can lead to 10^n reactions

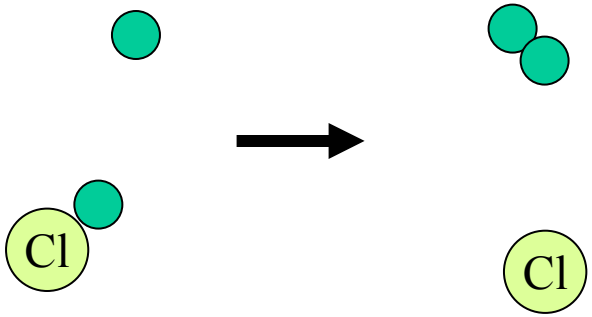
Chlorine-Catalyzed Ozone Destruction

Step 1: Cl Atom Reaction with Ozone



$$Cl + O_3 = ClO + O_2$$

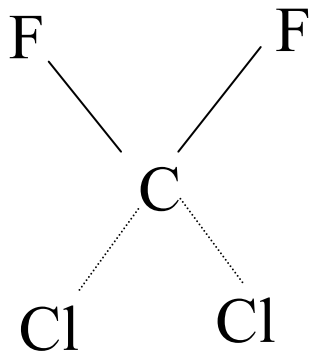
Step 2: Cl Atom Release



$$\begin{array}{r} ClO + O = Cl + O_2 \\ \hline O_3 + O = O_2 + O_2 \end{array}$$

Goes on for 100,000 turnovers until Cl is rained out as HCl

Chlorofluorocarbons: wonder molecules



Freon R-12

Chemically unreactive, inert
Uses: Refrigerants, circuit board cleaners, foam blowing agent
Much better than ammonia
Production: 500 kTons/yr in 1987
Lifetime in Atmosphere: 122 years

The Heroes

And they who bettered life on earth by new found mastery

Rowland now says that he knew, before he published his 1974 study showing the lethal connection between CFCs and ozone destruction, that the effect would be galvanic. After he and Molina realized the magnitude of their discovery, they hesitated at the brink.

"In our knowledge, the bottom had just dropped out. We'd just found out about the chain reaction, and realized that a major, possibly unavoidable, catastrophe already had been committed."

They talked to Hal Johnston, the UC Berkeley scientist who had warned about environmental damage from the American supersonic transport airplane. He confirmed their numbers.

"Johnston had caught the flak in 1971, and the question he posed as we walked out the door was, 'Are you ready for the heat?' And you say, 'sure,' but you don't know what the temperature really is going to be. It is somewhat disconcerting to be attacked."

Rowland and Molina were attacked, by the aerosol industry, by companies that manufactured CFCs, by scientists who worked for those companies, and even by President Ronald Reagan's Environmental Protection Agency chief Anne Burford, who dismissed their theory as a scare tactic. While the scientific community quickly came to agree with Rowland and Molina and the lay public voted with its dollars - sales of aerosol products began dropping quickly - the $2 billion per year CFC industry successfully continued for years to press its view that the CFC-ozone connection was unproved.

Even today, Rowland says, "there is a very active group […] in the House of Representatives who take the view that all of this is political. They have the attitude that Sweden is under the control of radical environmentalists and the Nobel Prize is just part of their program."
Rowland's daughter, University of Chicago art historian Ingrid Rowland, remembers those years as providing "not a great education in human nature" but one that has informed her own professional pursuits, particularly when she worked on a historical period that involved Machiavelli. "I saw what industry was willing to do to save money."

Once, she said, she and her mother were sitting behind two chemical company executives at a conference when discussion arose about a chemical process that, theoretically, could seriously damage the ozone layer in a very short time. The two executives began crowing and slapping each other on the back because the chemical, for a change, wasn't theirs. "It was the most terrible spectacle," she recalls.

The pressure from the aerosol industry even extended to an attempt to get him fired, Sherry Rowland said. "They wrote to Chancellor Dan Aldrich basically saying, 'You've got to shut that guy up.' Of course, they got a letter back, saying, 'He's doing what he's supposed to be doing. He certainly has freedom and I support him completely.'"

Rowland said many people have asked him whether winning the Nobel Prize had provided a vindication - "'vindication' is the word that is used" - after his years of attack from the CFC industry. It didn't feel quite like that, he says, because the scientific community had been supportive almost from the beginning, and that had meant that "You're not surrounded by naysayers; you're surrounded by people who are interested in looking at the quantitative details of it but not with the sense of shooting you down personally."

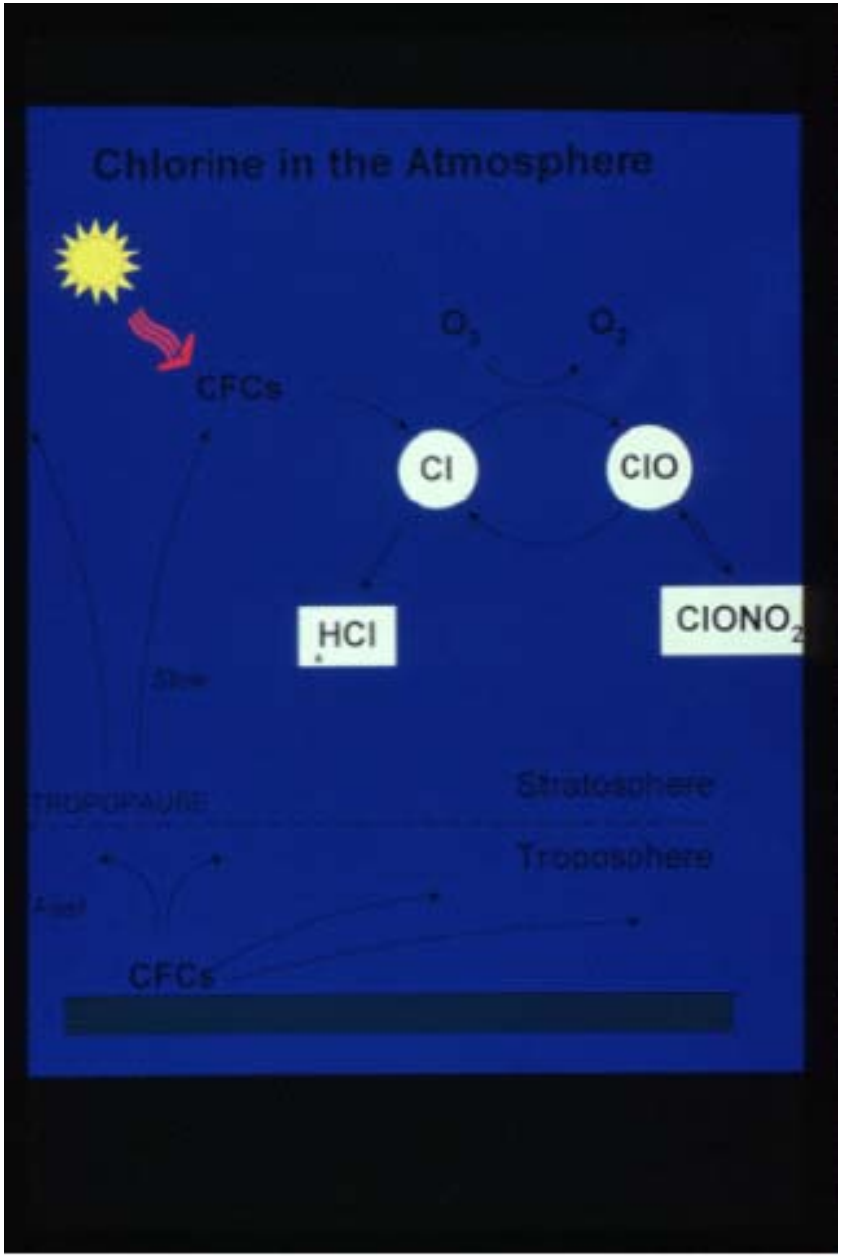
He adds that because science operates on finding things that earlier scientists have either overlooked or "botched," Rowland and his work now offer a challenge to future scientists. He accepts it. "Part of being a leader is also being a target."

Ingrid Rowland says that a hallmark of her father's character, and one she shares, is a remarkable optimism. "My mom's very good at smelling a rat," she said, but she and her father proceed through life expecting the best.

Such optimism shines through one of Rowland's 1993 comments to his fellow scientists: "We know from actual measurements in the atmosphere all over the world that the nations and industries and people of the world are complying with the terms of the Montreal Protocol.

The emissions of chlorofluorocarbons during the 1990s show a rapid decrease from the rates of the 1980s. Collectively, we have found out that it is possible to get international cooperation on a global scientific problem on the basis of scientific observation and consensus.

"Perhaps this global agreement can be a harbinger of the future; science and technology must play major roles in solving the problems we see all around us, and we all must continue to tell this not just to our colleagues, but to our representatives and to the general public, and we must be prepared to do it over and over again because the understanding is necessary.
"And it is still the most exciting game in town."



5) There they absorb UV and destroy ozone

4) 5-6 fold increase in Cl in atmosphere is largely attributed to CFC's

3) Catalytic cycle for ozone destruction

2) Rise into stratosphere

1) Mix in troposphere

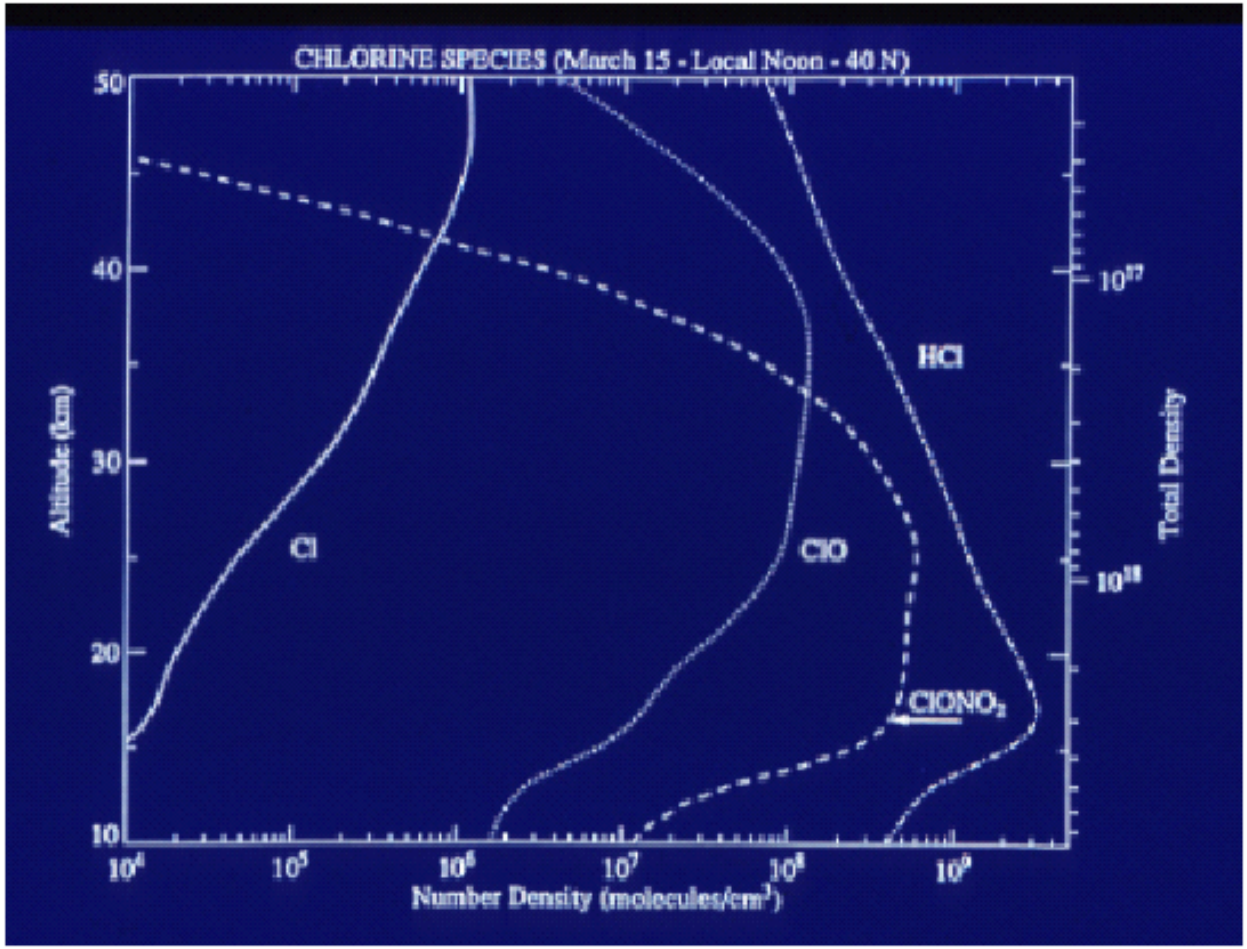
SST's were supposed to do this too but don't
Hal Johnston (CIT alum) at Berkeley in 1970's

Free Radicals Can Catalyze Ozone Destruction

Cl/ClO	Freons (CFC's)
Br/BrO	Fumigants, Oceans
NO/NO_2	SST's, natural N_2O
HO/HO_2	$H_2O + O(^1D)$ Reactions

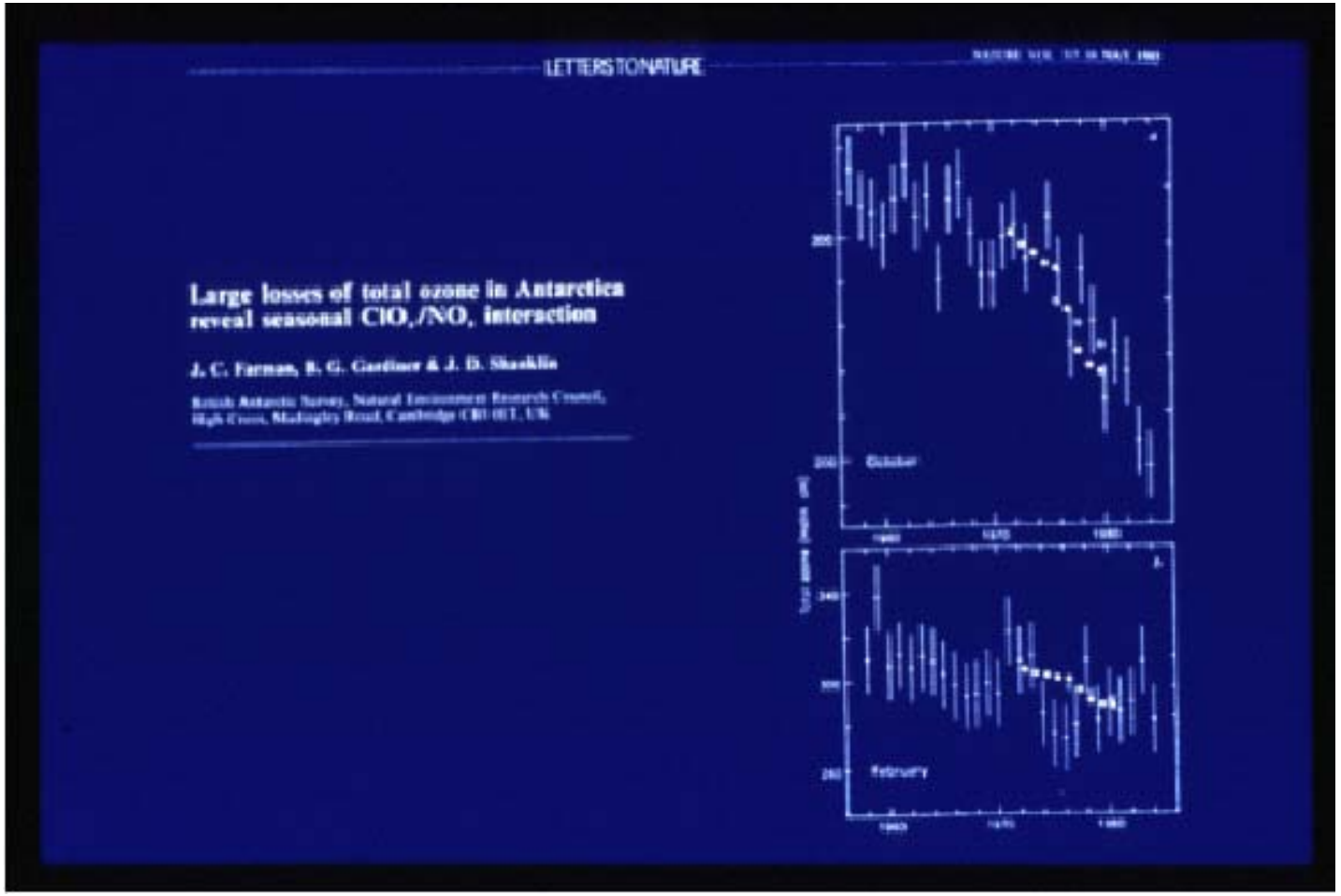
What's going on up there now

Things don’t seem so bad (yet)



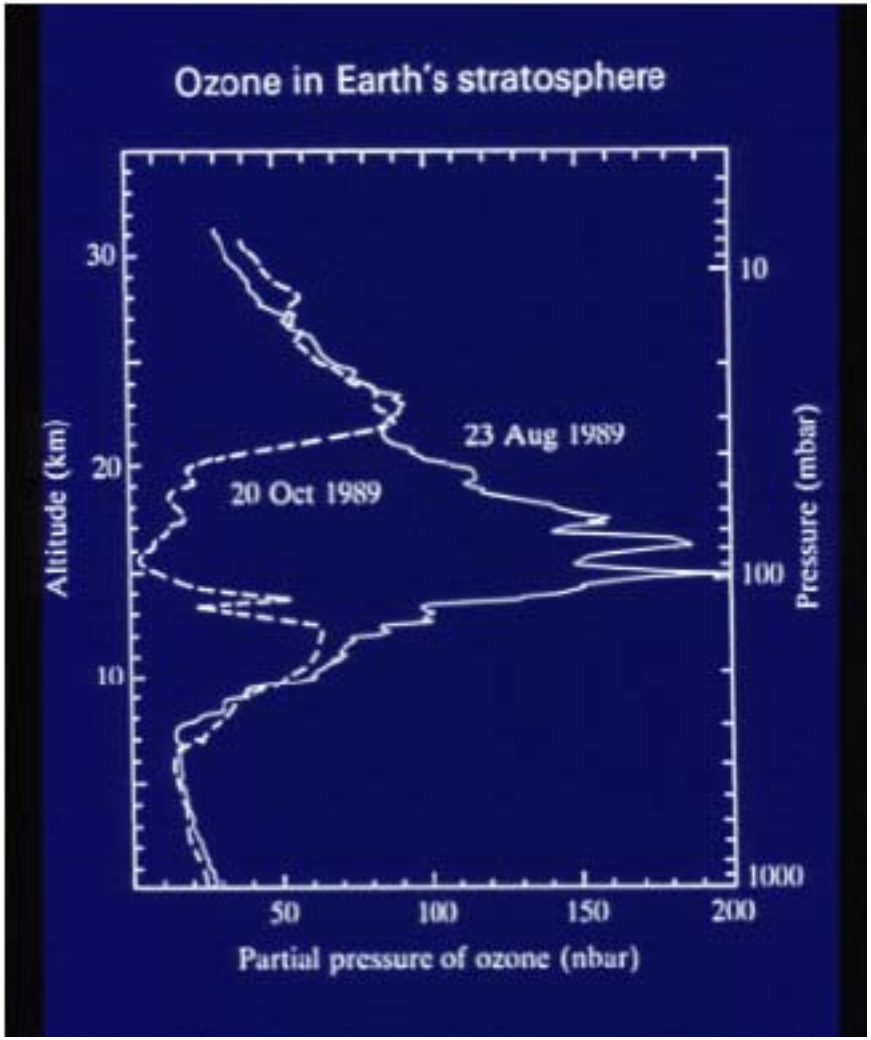
Cl and ClO 10-100 lower concentration than the reservoirs

The Fluke/Surprise of the Ozone Hole



NASA binned it out!

Balloon flights confirm ozone loss

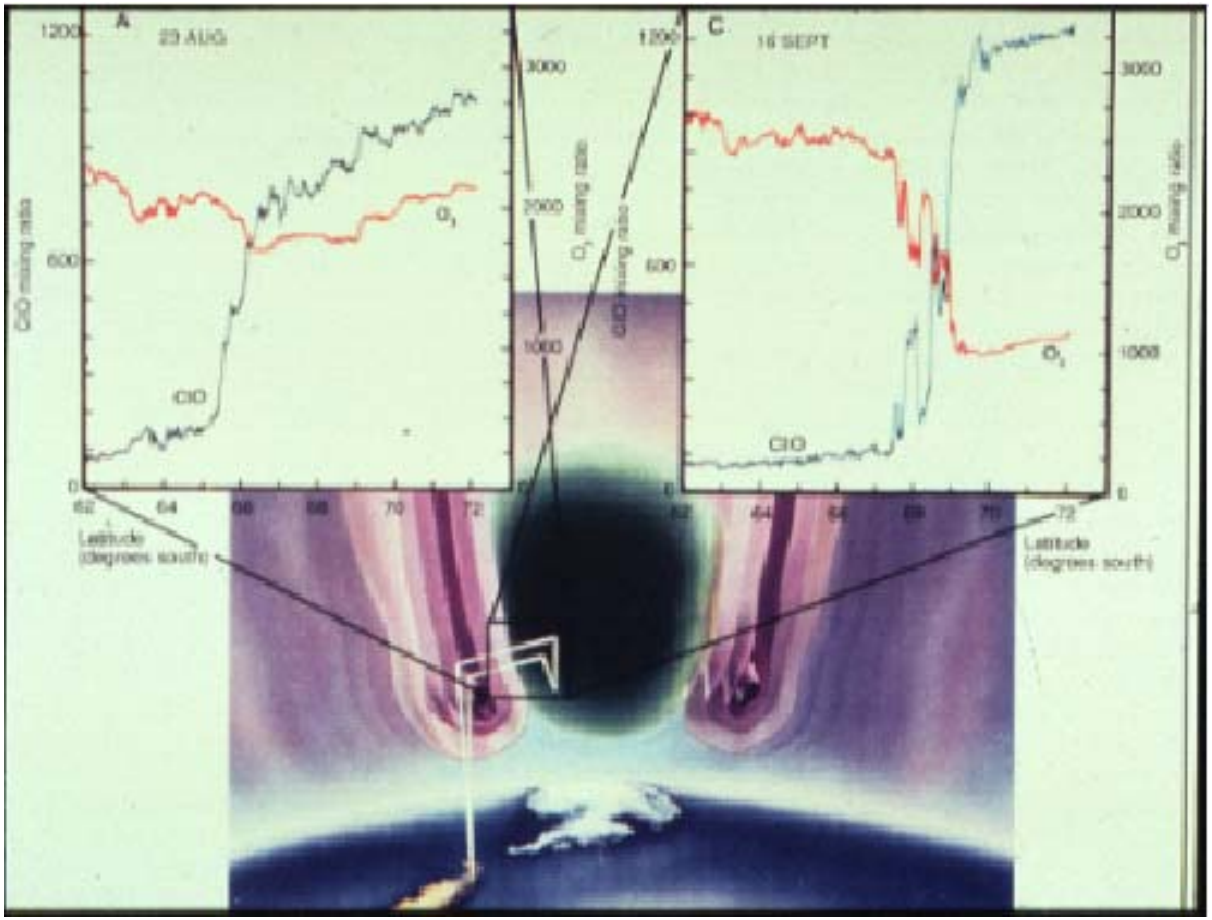


No one knows why

Flying Chem Lab

Jim Anderson/Harvard ER-2
Measures many species, including ClO, O_3

The Smoking Gun

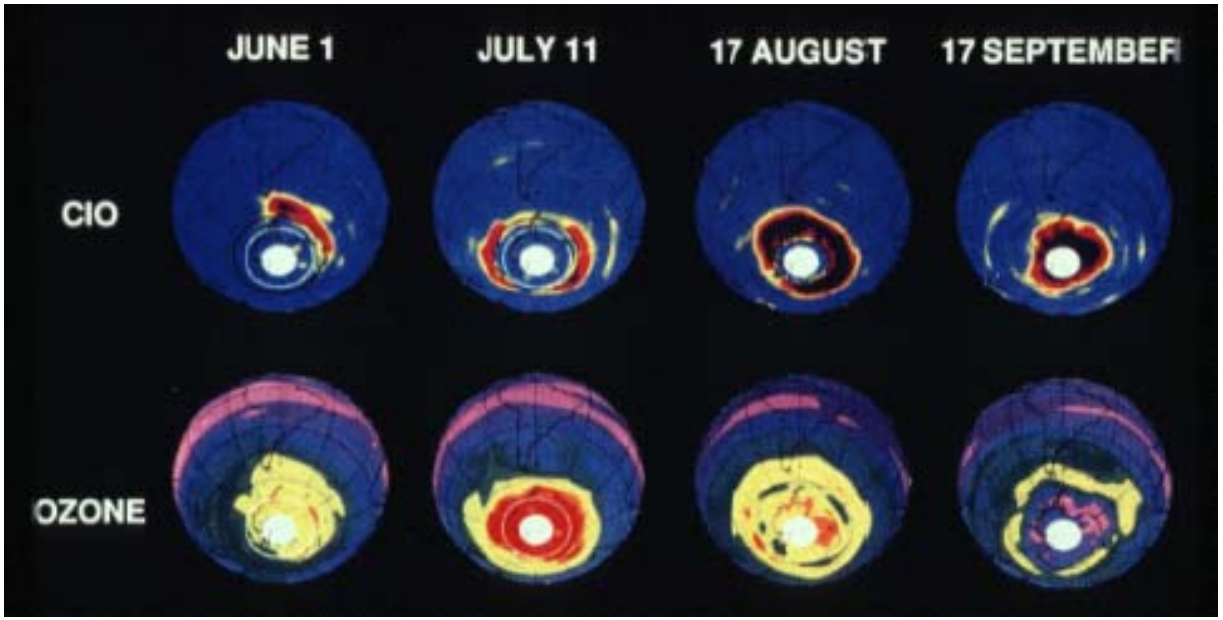


ClO up in Aug but O_3 not affected; ClO up in Sept and O_3 down
Even glitches are correlated

NASA Gets Into the Act

Upper Atmosphere Research Satellite
Launched from Space Shuttle in 1991

Microwave Limb Sounder/JPL



Obvious Ozone Depletion!

Winter: ClO builds up; ozone still high
air trapped in vortex very cold (200 K) mostly darkness
Spring: Temperature warms up slightly, sun rises
dramatic ozone loss, suggesting photochemical step
Eventually air warms up, breaks up polar vortex
Ozone-rich air mixes with polar air, eliminating ozone hole
Ozone-depleted air patches have been observed to drift northwards

The Facts to Reckon With

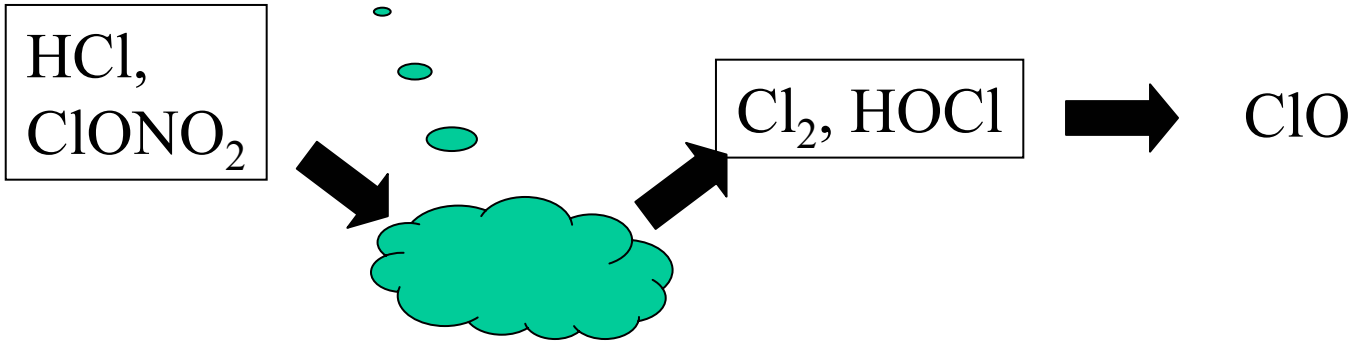
	Polar Winter	**Polar Spring**
Temperature	Low (min T<200K)	Warmer Temperature
Sunlight	Low levels	Increasing
Vortex	Confines cold air	persists in early spring
ClO	Abnormally high	Abnormally high
Ozone	Relatively unchanged	Abnormally low

Why missed previously?
Two major processes, one photochemical
Unique to Polar Regions

Polar *Stratospheric* Clouds

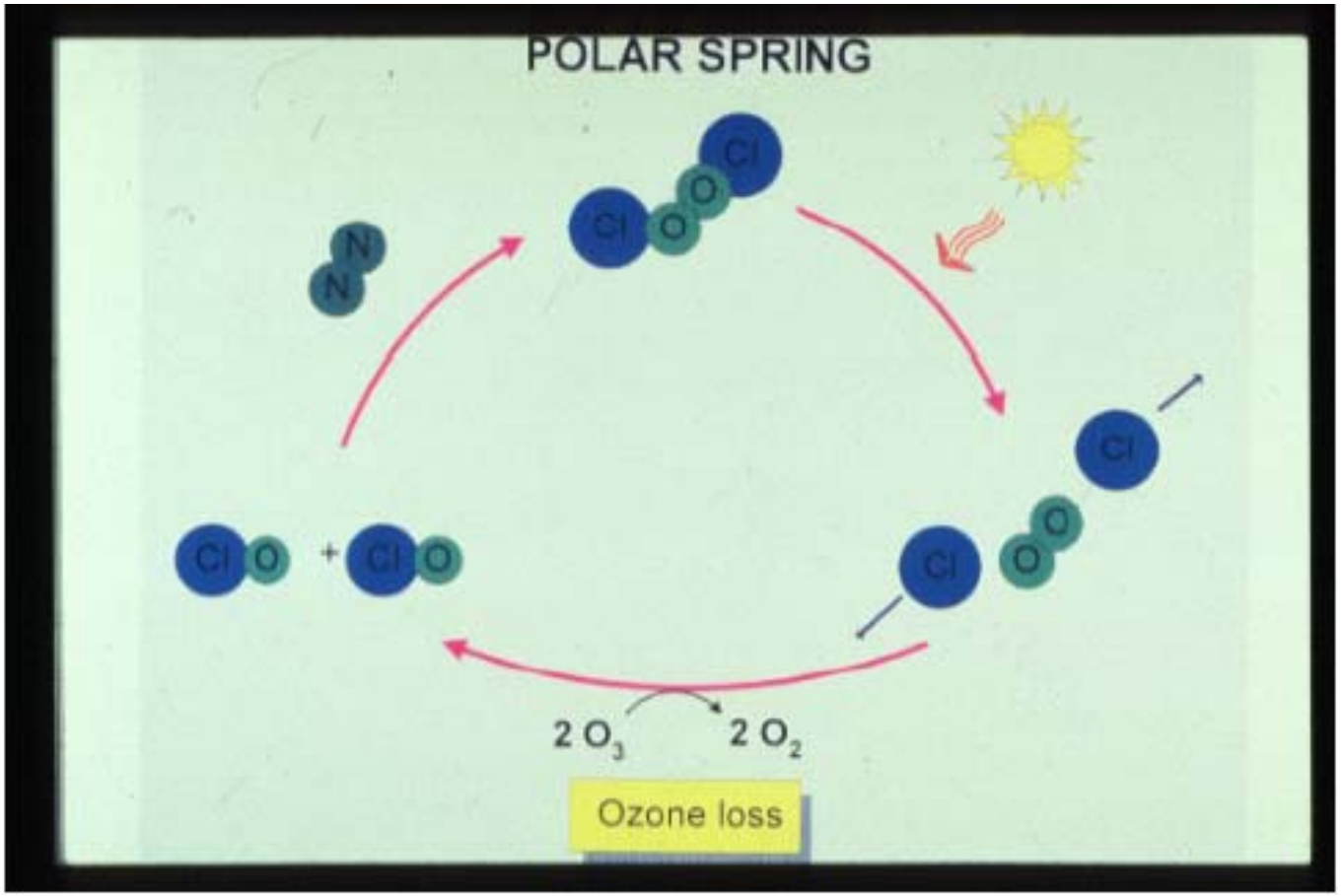
Hardly ever see water in stratosphere
Water density only 1 ppm
Too dilute to condense water
But T=187 K in Polar Vortex in winter; reaches frost point

Polar Winter
Reactions on Polar Stratospheric Clouds



Type I Nitric Acid/Water
Type II Water Ice

- Reservoir compounds, HCl and $ClONO_2$
  react on Surface of Cloud Particles to Produce Cl, HOCl, ClO
- These Destroy Ozone Catalytically
- But, even this isn't enough to account for magnitude of hole

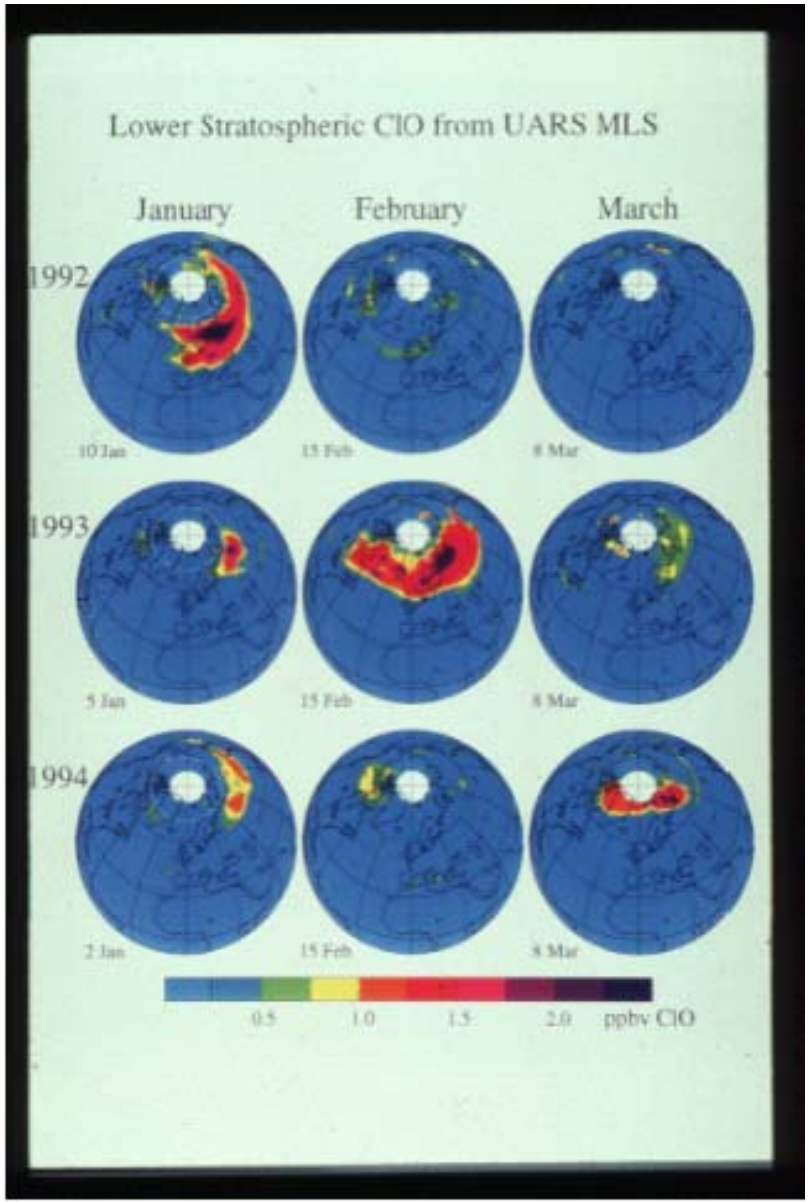


ClO can't absorb enough light

But ClO+ ClO=ClO-OCl (dimer)

That does absorb, forms Cl atoms, which destroy ozone

Maggie Tolbert, another CIT alum, now at CU Boulder



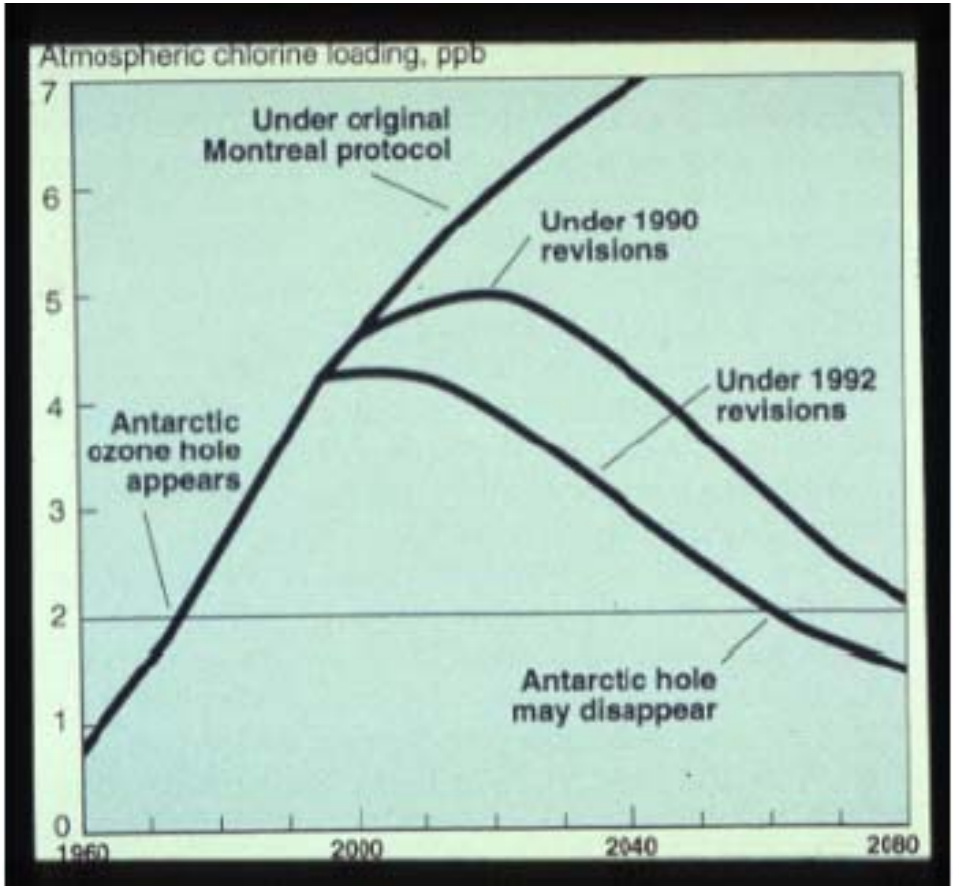
Also see hole in northern hemisphere

Lots more ozone here already

Smooths out lump

Vortex doesn't persist as long in north pole either

Montreal Protocol

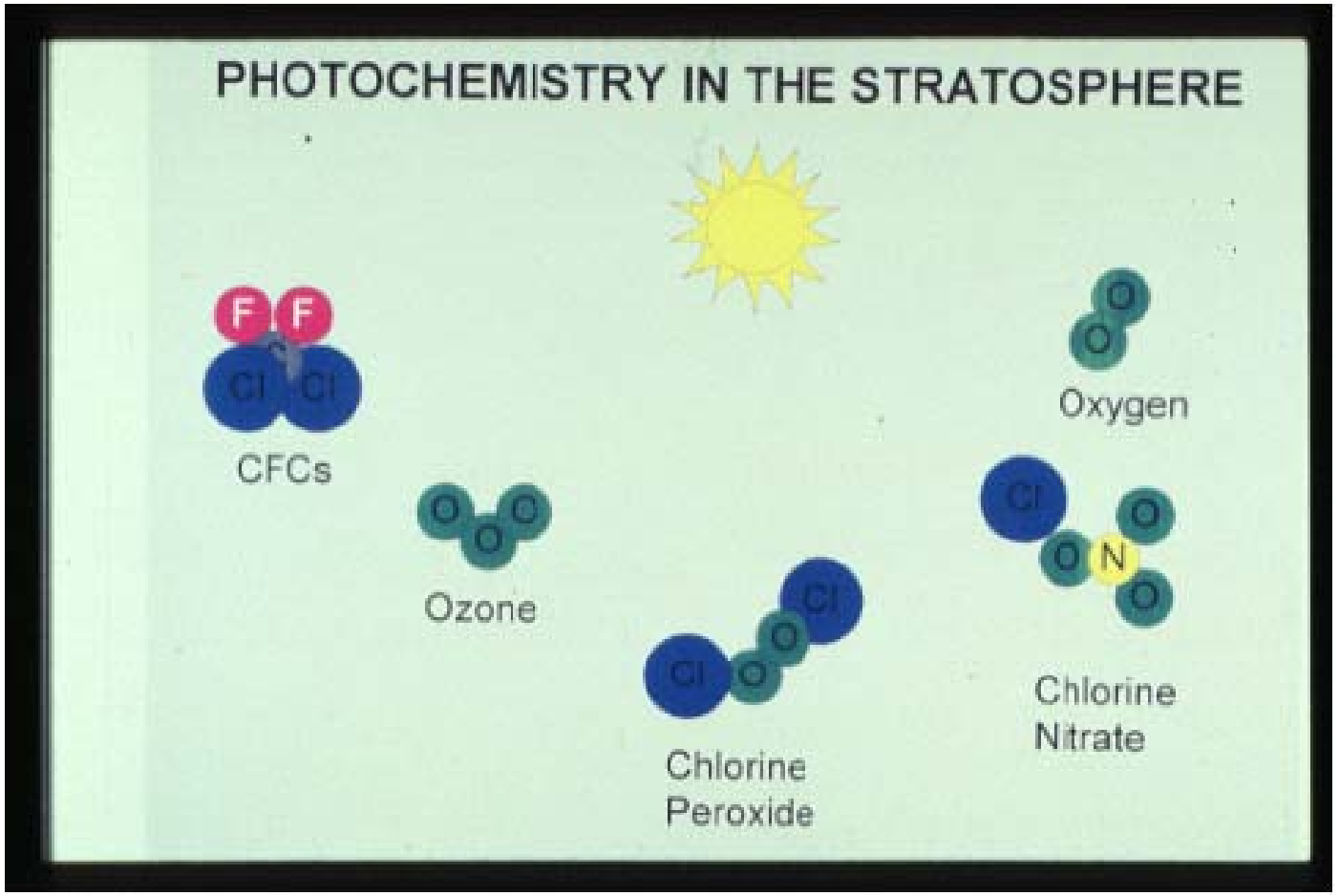


DuPont phases out CFC's early
U.S. asks them to keep making it
Rush Limbaugh claims "scientific conspiracy"
Arizona claims "sham"

What to do to fix the problem?

- Use CFC's that aren't as inert
- Don't reach the stratosphere
- Thus don't deplete ozone
- Don't work as well as refrigerants
- Requires retrofitting existing systems/expensive
- I've got my stash of R-12, R-22!

Moral to the story



8 electrons are great, but know your chemistry!