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

Richard S. Stolarski

NASA Goddard Space Flight Center Emeritus

A few background facts

- **Ozone in atmosphere "discovered" by measurement of cutoff of solar spectrum in UV**
- **Ozone determined to be a layer at high altitude (in stratosphere)**
- **Ozone column amount quantitatively measured by UV absorption**
- **First ozone theory by Chapman (1930)**

Ozone Photochemistry

Odd Oxygen (O atoms + O_3 molecules)

Chapman Theory 1930

Initiation: $h\nu + O_2 \text{--->} O + O$

($\lambda < 240$ nm)

Propagation: $O + O_2 + M \text{--->} O_3 + M$

$h\nu + O_3 \text{--->} O_2 + O$

($200 \text{ nm} < \lambda < 300 \text{ nm}$)

Termination: $O + O_3 \text{--->} O_2 + O_2$

Sydney Chapman

Ozone is continuously being made and destroyed in the atmosphere

But there is a lot of laboratory background that underlies Chapman's theory of stratospheric ozone

- **Laboratory ozone decomposition experiments (circa 1900-1930)**
  - **Ozone obtained from pure oxygen by e.g. electric discharge**
  - **Ozone change measured by pressure change ($2O_3 \rightarrow 3O_2$)**
  - **Ozone change studied as a function of:**
    - **Temperature**
    - **Visible light**
    - **UV light**
    - **Contaminant gases (i.e. water, chlorine)**

Catalysis Accelerates Termination Reaction

Hydrogen oxides, Nitrogen oxides

Chlorine oxides, Bromine oxides

Example: Chlorine

$Cl + O_3 \text{--->} ClO + O_2$

$ClO + O \text{--->} Cl + O_2$

$O + O_3 \text{--->} O_2 + O_2$ **net**

Fritz Weigert first studied the impact of chlorine on ozone decomposition his laboratory in 1907

A few of the many references to chlorine-ozone studies in the laboratory

Allmand, A. J.,and J.W. T. Spinks,The action of light on mixtures of ozone and chlorine, 1, Experimental results with low ozone concentration, J. Chem. Soc., 1652, 1931.

Allmand, A.J., and J.W.T. Spinks, The action of light on mixtures of ozone and chlorine, 2, Results with high ozone concentrations: Discussion, J. Chem. Soc., 599, 1932.

Norrish, R. G. W., and G. H. J. Neville, The decomposition of ozone photosensitized by chlorine, J. Chem.Soc., 1864, 1934

Johnston, H. S., E. D. Morris, Jr., and J. Van den Bogaerde, Molecular modulation kinetic spectrometry: ClOO and ClO2 radicals in the photolysis of chlorine in oxygen, J. Amer. Chem. Soc., 91, 7712, 1969.

The Nobel Prize in Chemistry 1967

Manfred Eigen, Ronald G.W. Norrish, George Porter

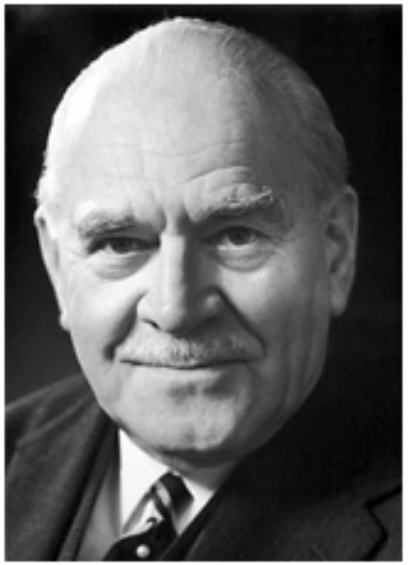
The Nobel Prize in Chemistry 1967

Manfred Eigen

Ronald G.W. Norrish

George Porter

Manfred Eigen



Ronald George Wreyford 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 equlibrium by means of very short pulses of energy"*.

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

Stedman, circa 1972: "Chlorine destroys ozone; everybody knows that!"

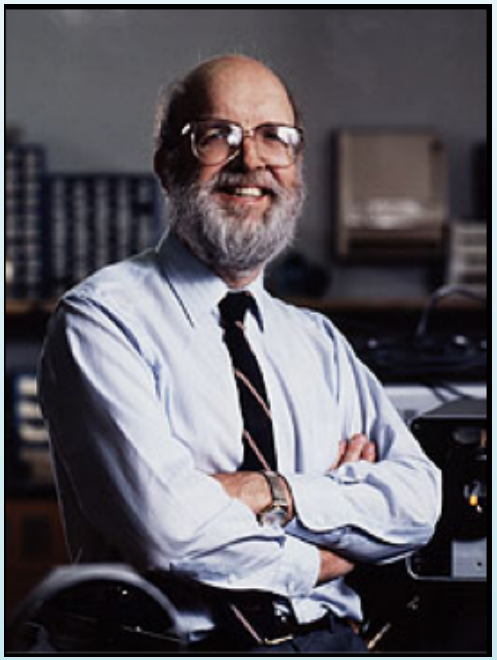
NASA CR-129003

ASSESSMENT OF POSSIBLE ENVIRONMENTAL EFFECTS OF SPACE SHUTTLE OPERATIONS

By R.J. Cicerone, D. H. Stedman, R. S. Stolarski, A. N. Dingle, and R. A. Cellarius

University of Michigan
Department of Electrical and Computer Engineering
Space Physics Research Laboratory
Ann Arbor, Michigan

June 1973



How did we come to know about the importance of CFCs?

Article

Nature **249**, 810-812 (28 June 1974) | doi:10.1038/249810a0

Stratospheric sink for chlorofluoromethanes: chlorine atomc-atalysed destruction of ozone

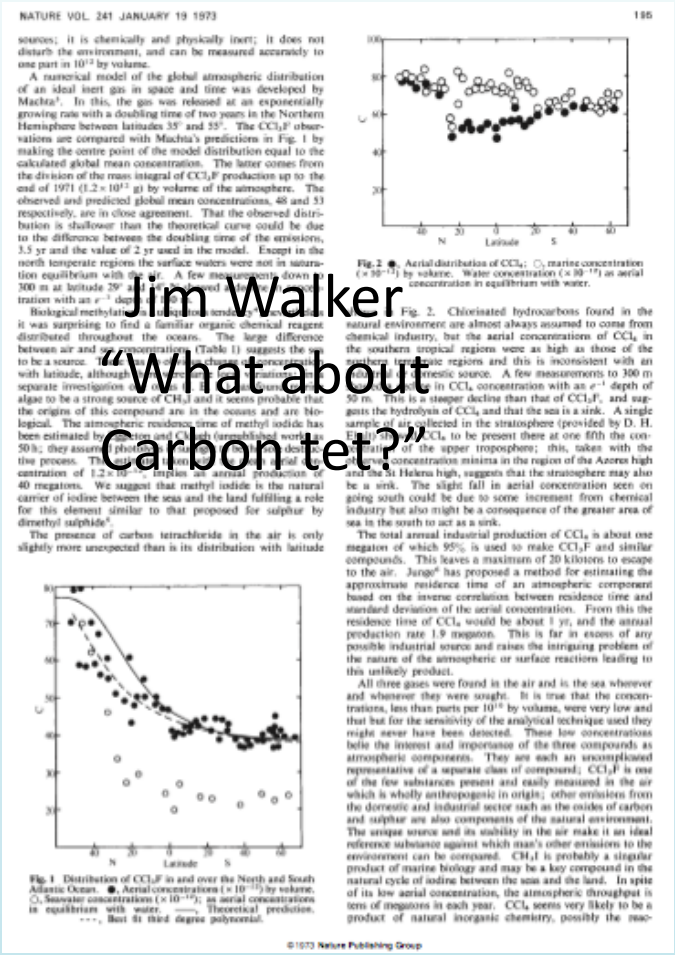
Mario J. Molina & F. S. Rowland

1. Department of Chemistry, University of California, Irvine, California 92664

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!

Lovelock et al. Nature, 1973



NATURE VOL. 241 JANUARY 19 1973 195

sources; it is chemically and physically inert; it does not disturb the environment, and can be measured accurately to one part in 10^{12} by volume.

A numerical model of the global atmospheric distribution of an ideal inert gas in space and time was developed by Machta[5]. In this, the gas was released at an exponentially growing rate with a doubling time of two years in the Northern Hemisphere between latitudes 35° and 55°. The CCl_3F observations are compared with Machta's predictions in Fig. 1 by making the centre point of the model distribution equal to the calculated global mean concentration. The latter comes from the division of the mass integral of CCl_3F production up to the end of 1971 (1.2×10^{12} g) by volume of the atmosphere. The observed and predicted global mean concentrations, 48 and 53 respectively, are in close agreement. That the observed distribution is shallower than the theoretical curve could be due to the difference between the doubling time of the emissions, 3.5 yr and the value of 2 yr used in the model. Except in the north temperate regions the surface waters were not in saturation equilibrium with the air. A few measurements down to 300 m at latitude 29° [illegible] tration with an e^{-1} de[illegible]

Biological methylat[illegible] it was surprising to find a familiar organic chemical reagent distributed throughout the oceans. The large difference between air and [illegible] concentrations (Table 1) suggests the sea to be a source. T[illegible] with latitude, although [illegible] separate investigation [illegible] algae to be a strong source of CH_3I and it seems probable that the origins of this compound are in the oceans and are biological. The atmospheric residence time of methyl iodide has been estimated by [illegible] and CCl_4 (unpublished work) as 50 h; they assum[illegible] tive process. Th[illegible] centration of $1.2 \times 10^{-[illegible]}$ implies an annual production of 40 megatons. We suggest that methyl iodide is the natural carrier of iodine between the seas and the land fulfilling a role for this element similar to that proposed for sulphur by dimethyl sulphide[8].

The presence of carbon tetrachloride in the air is only slightly more unexpected than is its distribution with latitude

Fig. 1 Distribution of CCl_3F in and over the North and South Atlantic Ocean. ●, Aerial concentrations ($\times 10^{-12}$) by volume. ○, Seawater concentrations ($\times 10^{-12}$); as aerial concentrations in equilibrium with water. ——, Theoretical prediction. - - -, Best fit third degree polynomial.

Fig. 2 ●, Aerial distribution of CCl_4; ○, marine concentration ($\times 10^{-12}$) by volume. Water concentration ($\times 10^{-12}$) as aerial concentration in equilibrium with water.

Fig. 2. Chlorinated hydrocarbons found in the natural environment are almost always assumed to come from chemical industry, but the aerial concentrations of CCl_4 in the southern tropical regions were as high as those of the northern temperate regions and this is inconsistent with an industrial domestic source. A few measurements to 300 m [illegible] in CCl_4 concentration with an e^{-1} depth of 50 m. This is a steeper decline than that of CCl_3F, and suggests the hydrolysis of CCl_4 and that the sea is a sink. A single sample of air collected in the stratosphere (provided by D. H. Ehhalt) [illegible] CCl_4 to be present there at one fifth the concentration of the upper troposphere; this, taken with the [illegible] concentration minima in the region of the Azores high and the St Helena high, suggests that the stratosphere may also be a sink. The slight fall in aerial concentration seen on going south could be due to some increment from chemical industry but also might be a consequence of the greater area of sea in the south to act as a sink.

The total annual industrial production of CCl_4 is about one megaton of which 95% is used to make CCl_3F and similar compounds. This leaves a maximum of 20 kilotons to escape to the air. Junge[6] has proposed a method for estimating the approximate residence time of an atmospheric component based on the inverse correlation between residence time and standard deviation of the aerial concentration. From this the residence time of CCl_4 would be about 1 yr, and the annual production rate 1.9 megaton. This is far in excess of any possible industrial source and raises the intriguing problem of the nature of the atmospheric or surface reactions leading to this unlikely product.

All three gases were found in the air and in the sea wherever and whenever they were sought. It is true that the concentrations, less than parts per 10^{10} by volume, were very low and that but for the sensitivity of the analytical technique used they might never have been detected. These low concentrations belie the interest and importance of the three compounds as atmospheric components. They are each an uncomplicated representative of a separate class of compound; CCl_3F is one of the few substances present and easily measured in the air which is wholly anthropogenic in origin; other emissions from the domestic and industrial sector such as the oxides of carbon and sulphur are also components of the natural environment. The unique source and its stability in the air make it an ideal reference substance against which man's other emissions to the environment can be compared. CH_3I is probably a singular product of marine biology and may be a key compound in the natural cycle of iodine between the sea and the land. In spite of its low aerial concentration, the atmospheric throughput is tens of megatons in each year. CCl_4 seems very likely to be a product of natural inorganic chemistry, possibly the reac-

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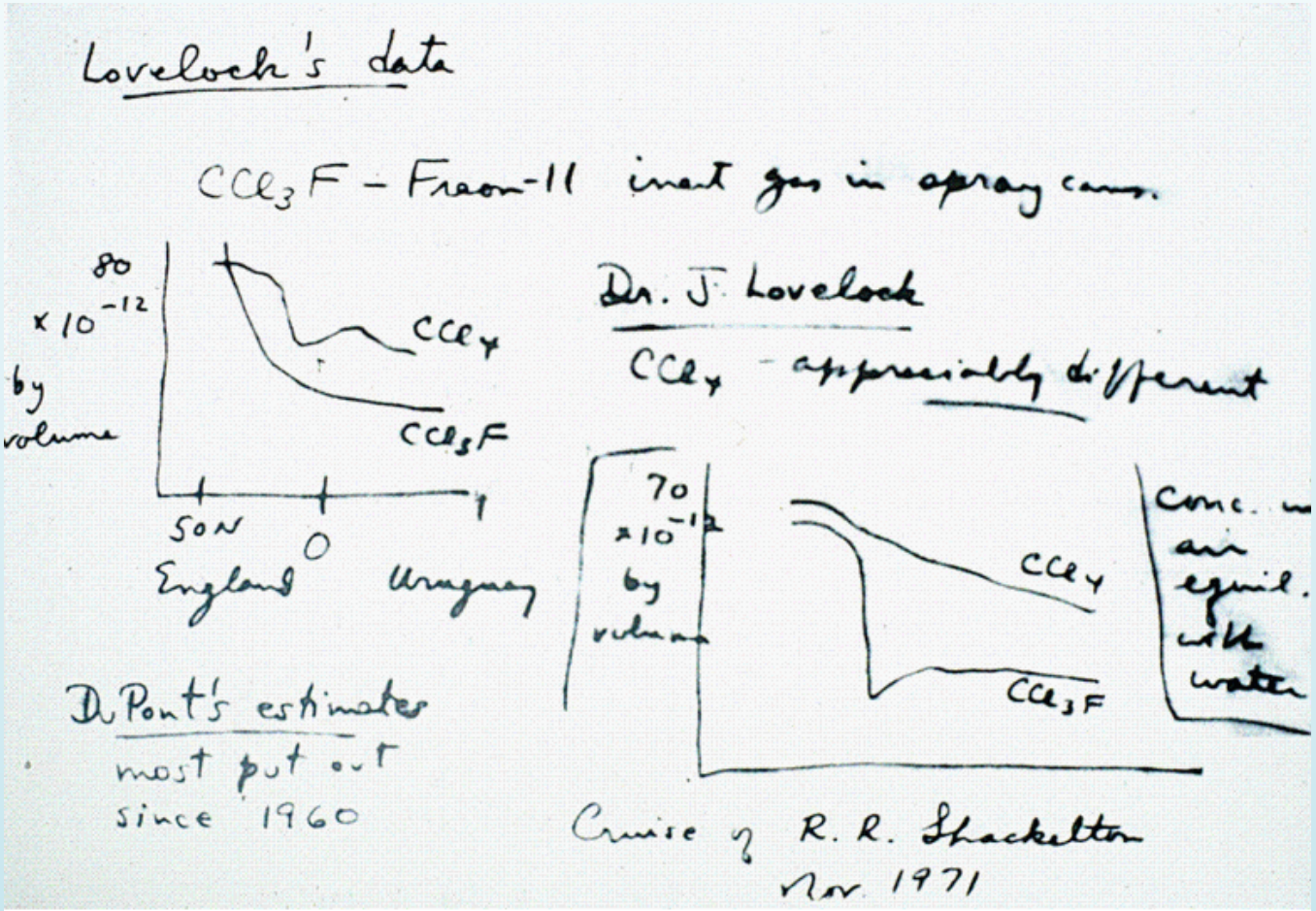
Jim Walker
"What about
Carbon tet?"

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."

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



Slide 1: Ft. Lauderdale, January 1972.

The Antarctic Ozone Hole

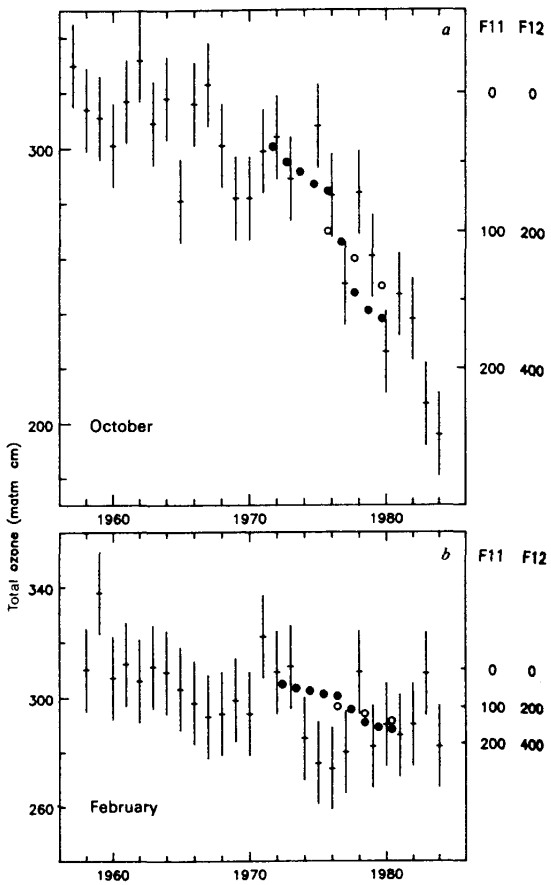
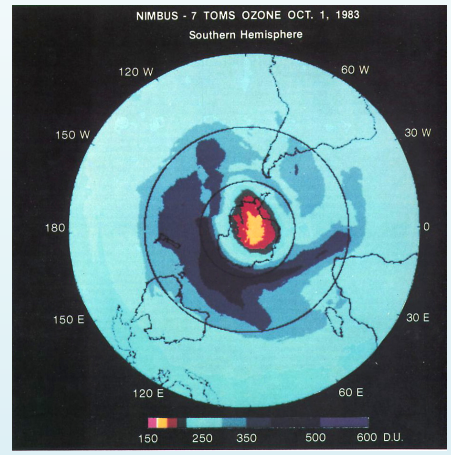


Fig. 2 Monthly means of total O_3 at Halley Bay, and Southern Hemisphere measurements of F-11 (●, p.p.t.v. (parts per thousand by volume) $CFCl_3$) and F-12 (○, p.p.t.v. CF_2Cl_2). *a*, October, 1957–84. *b*, February, 1958–84. Note that F-11 and F-12 amounts increase down the figure.

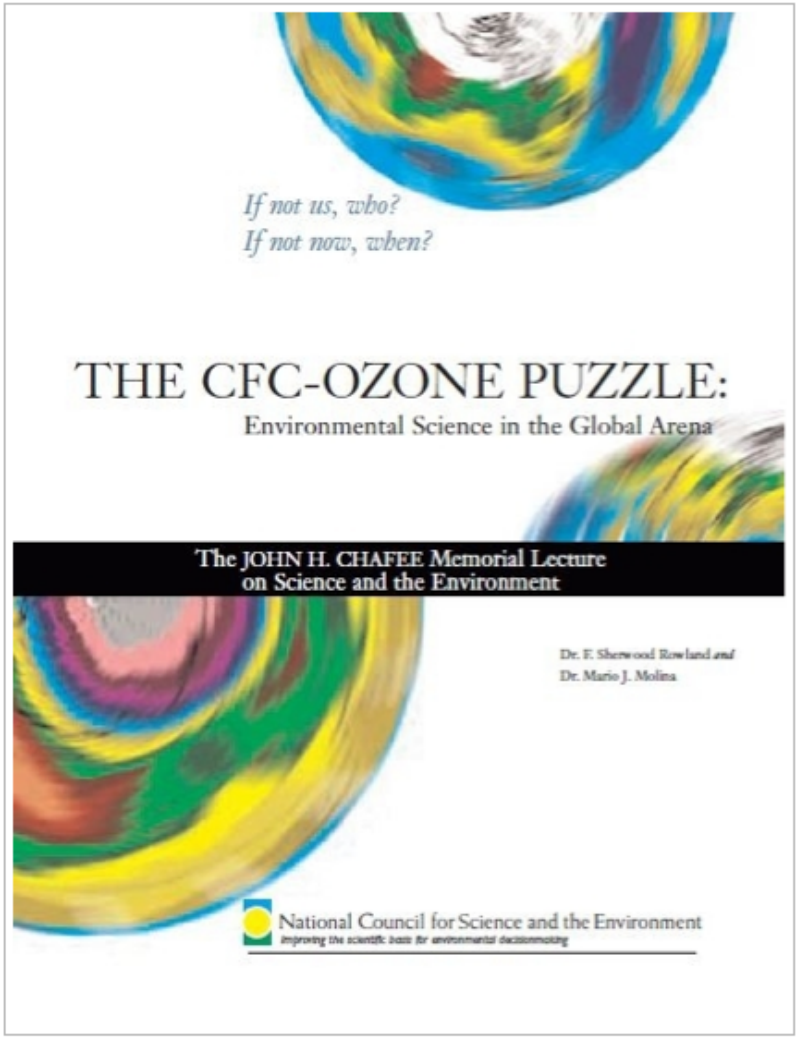


June 1985: Farman et al. paper published
July 1985: WMO/UNEP Ozone Assessment meeting
August 1985: Bhartia presentation at IAGA

Rowland: This observation by the British brought the NASA satellite people back to look at their data. Actually, they've gotten sort of a bad rap about it. What they did was program their data to reject, but notify, that some unusually low ozone values were being recorded. If you are getting unexpected low values when the instrument is working at the very limit of its detection, then you put that aside, saying, maybe there is something happening there that is real, but maybe it is an instrumental problem, and we'll have to go back and look at it carefully.

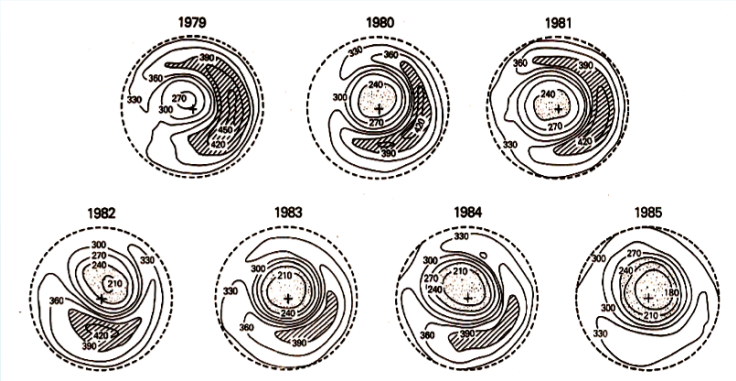
Ozone Depletion:

CFC–Ozone Puzzle: Lecture



http://WWW.EOEARTH.ORG/ARTICLE/CFC-OZONE_PUZZLE:_LECTURE?TOPIC=49594

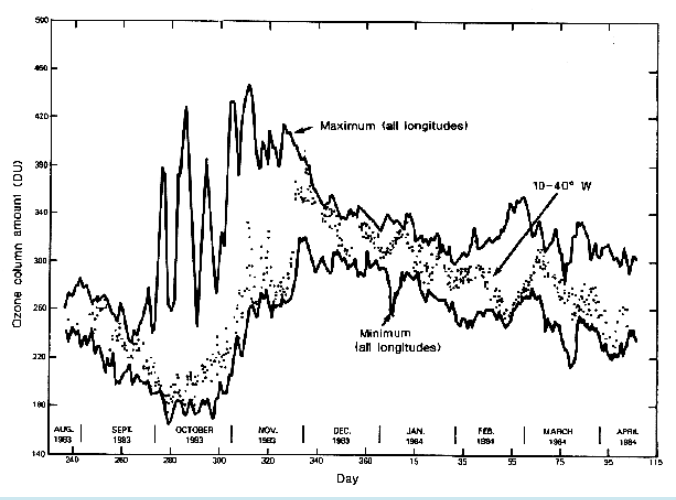
Figures from our 1986 Nature paper on the ozone hole

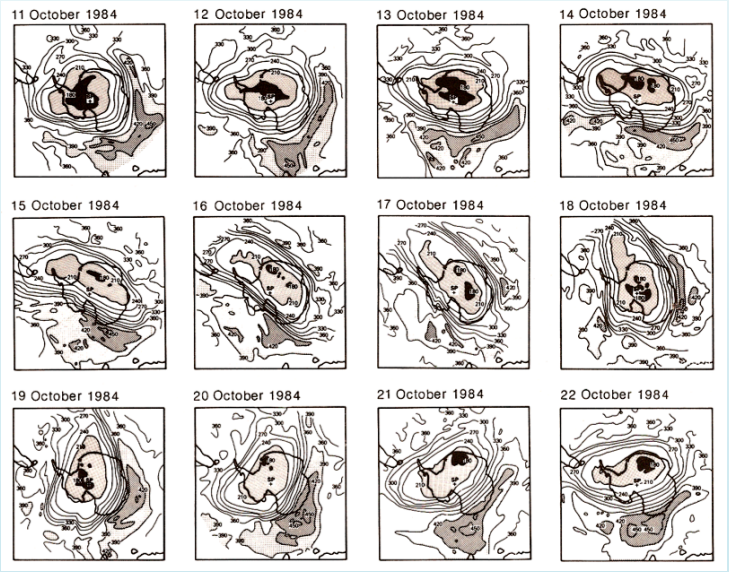


Nimbus 7 satellite measurements of the springtime Antarctic ozone decrease

R. S. Stolarski, A. J. Krueger, M. R. Schoeberl, R. D. McPeters, P. A. Newman & J. C. Alpert*

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





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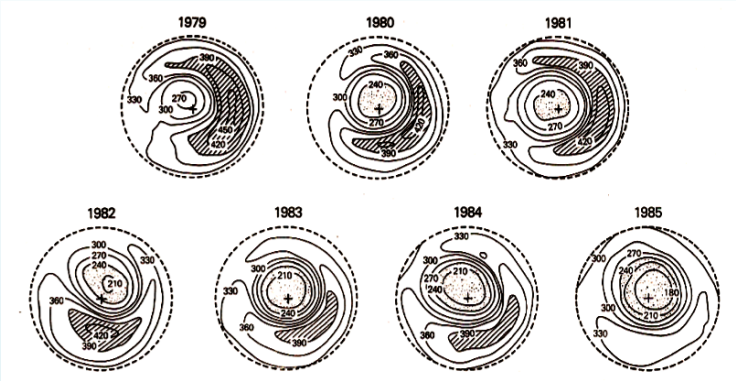

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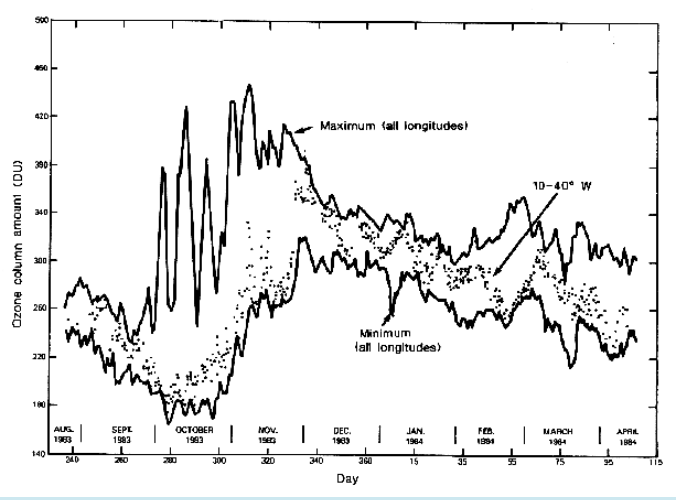
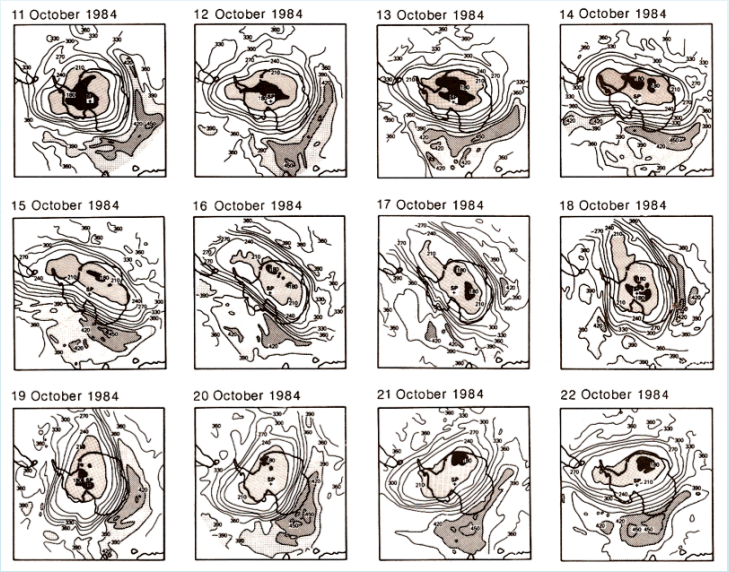




What about the theory of the ozone hole?

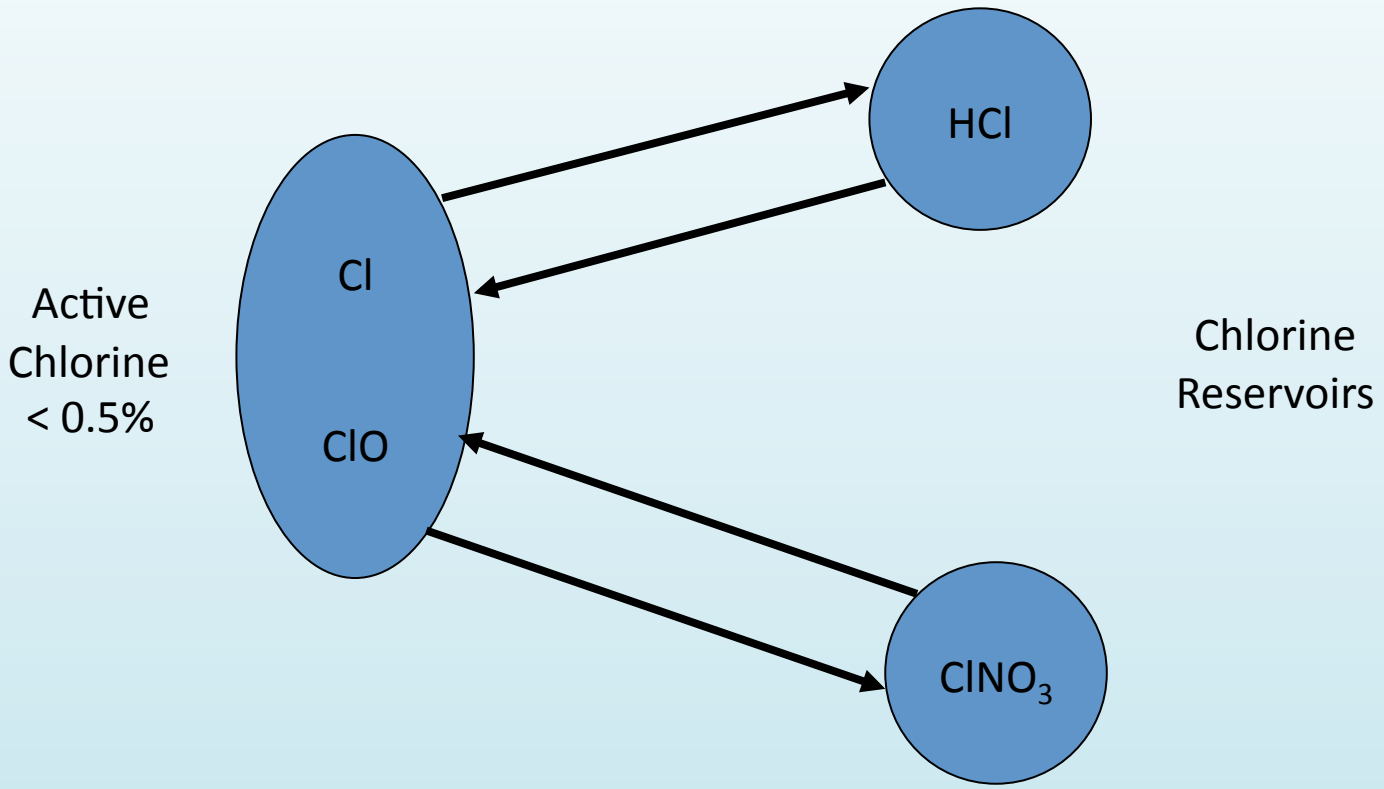
Feldafing Workshop, June 1984

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. $ClONO_2$ 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)



Polar Stratospheric Clouds (PSCs)

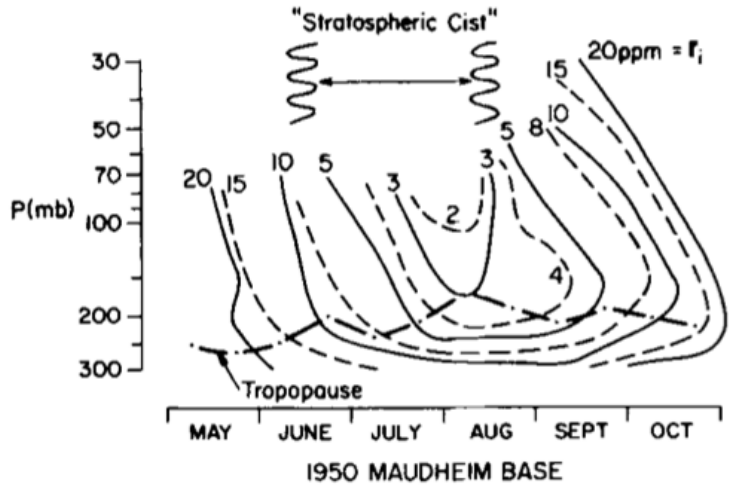


Fig. 1. Saturation mixing ratios of water vapor with respect to ice (in ppm, i.e. units of 10^{-6} g H_2O/g air) vs pressure for Maudheim base (70°03′S, 10°56′W) during the 1950 Antarctic winter. The curves extend up to the bursting level of the balloons. The temperature data used were half-monthly means. 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*, 530–534

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

Thin, persistent very high clouds called "Stratospheric Cist" were reported at Maudheim base (71°03′S, 10°56′W) during the 1950–51 austral winters. The nature of these clouds, whether they are H_2O 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

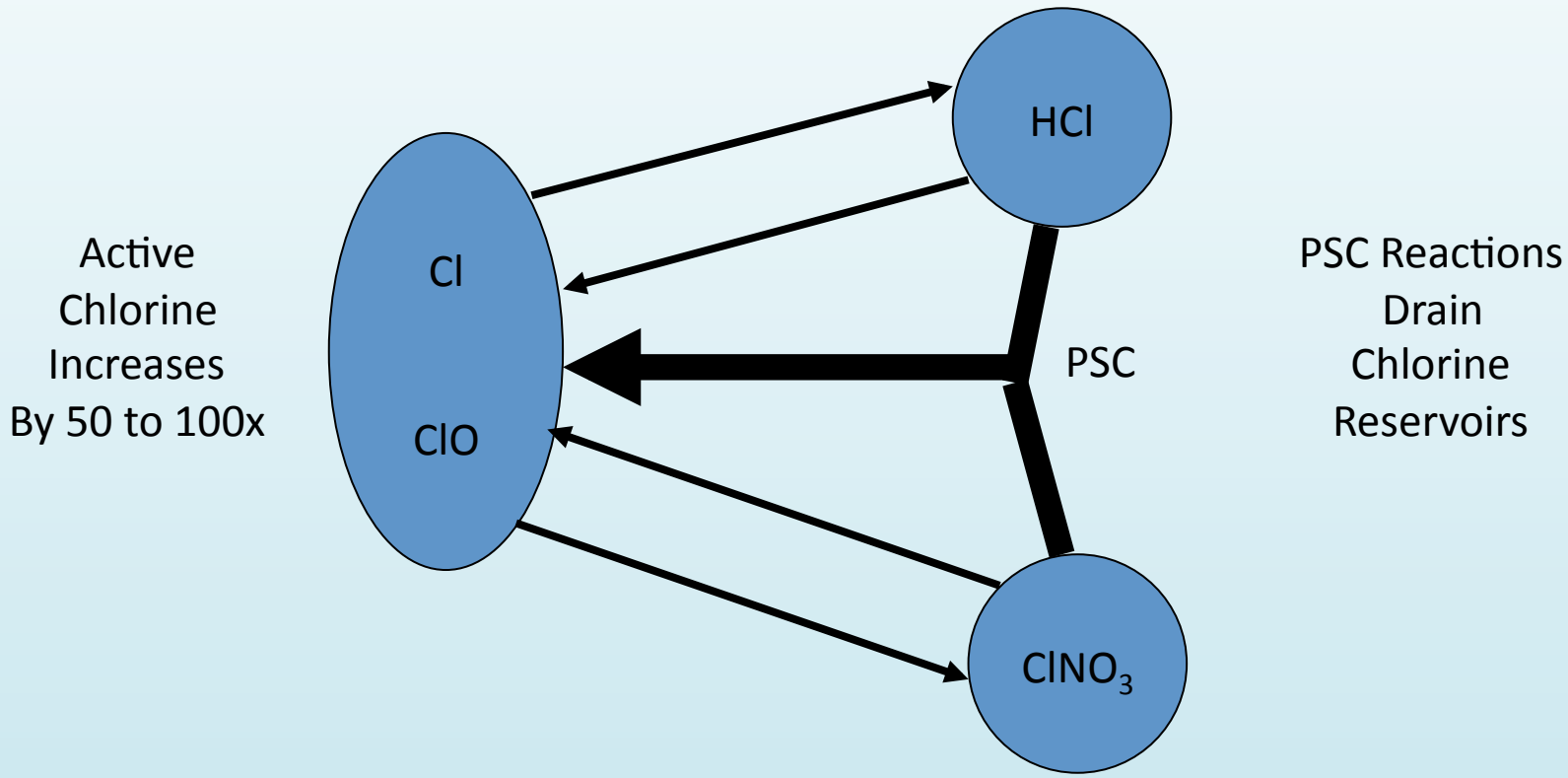
A Model of the Antarctic Sink for Stratospheric Water Vapor

ANNE R. DOUGLASS[1] 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 H_2O 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 1973 Antarctic winter stratosphere, initial water vapor mixing ratios of 2.7 and 3.0 ppmm lead to removal of 1.6 and 2.7 × 10^{10} kg H_2O from the lower stratosphere. This annual sink magnitude is small, representing about 2% of the total stratospheric H_2O burden and about 10% of the apparent sink identified by Ellsaesser (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.

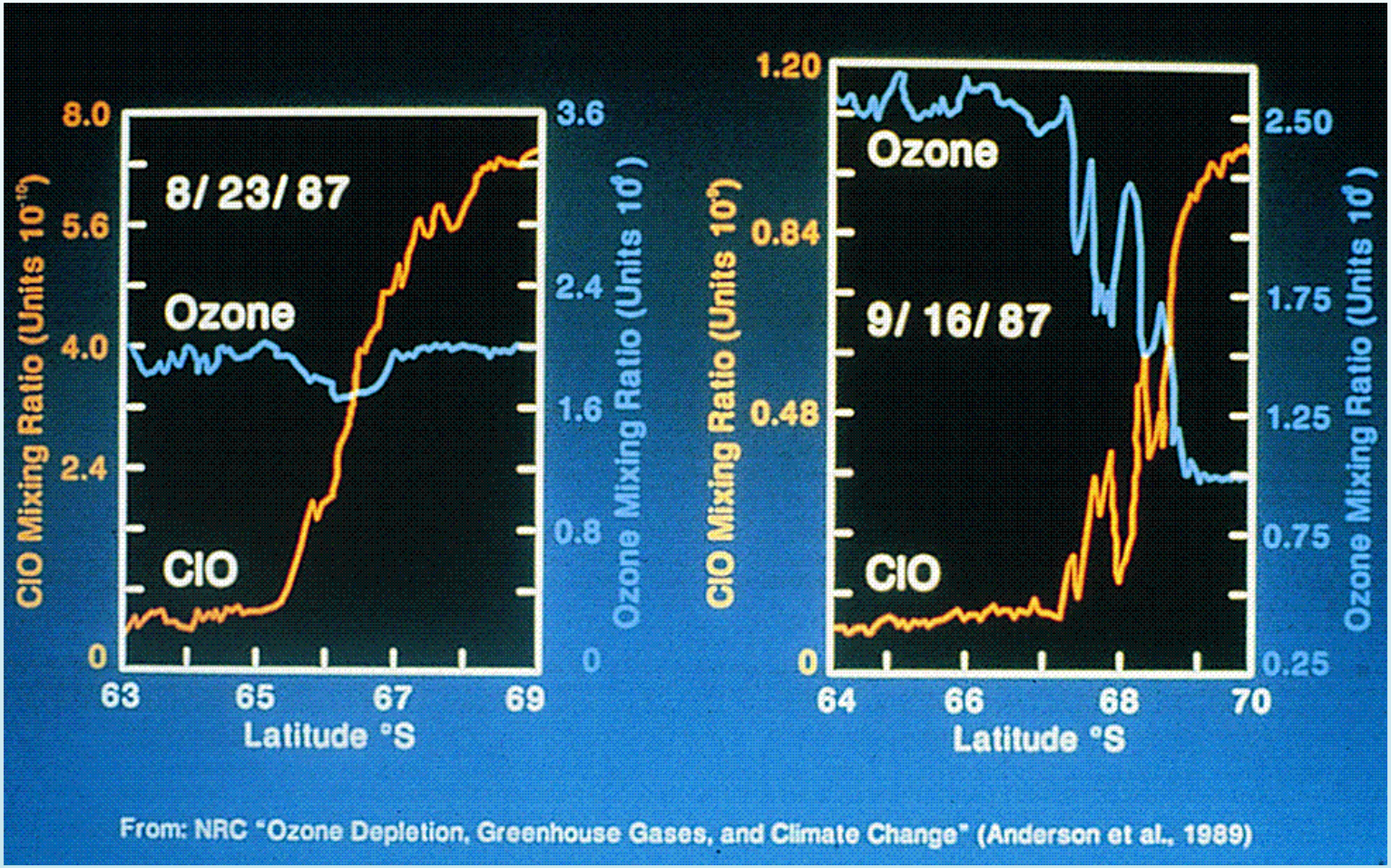
Chlorine Photochemistry (polar)



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 – NOx chemistry variations induced by solar cycle- required N2O change that was not observed.**
- **Other?**

“Smoking Gun Slide”



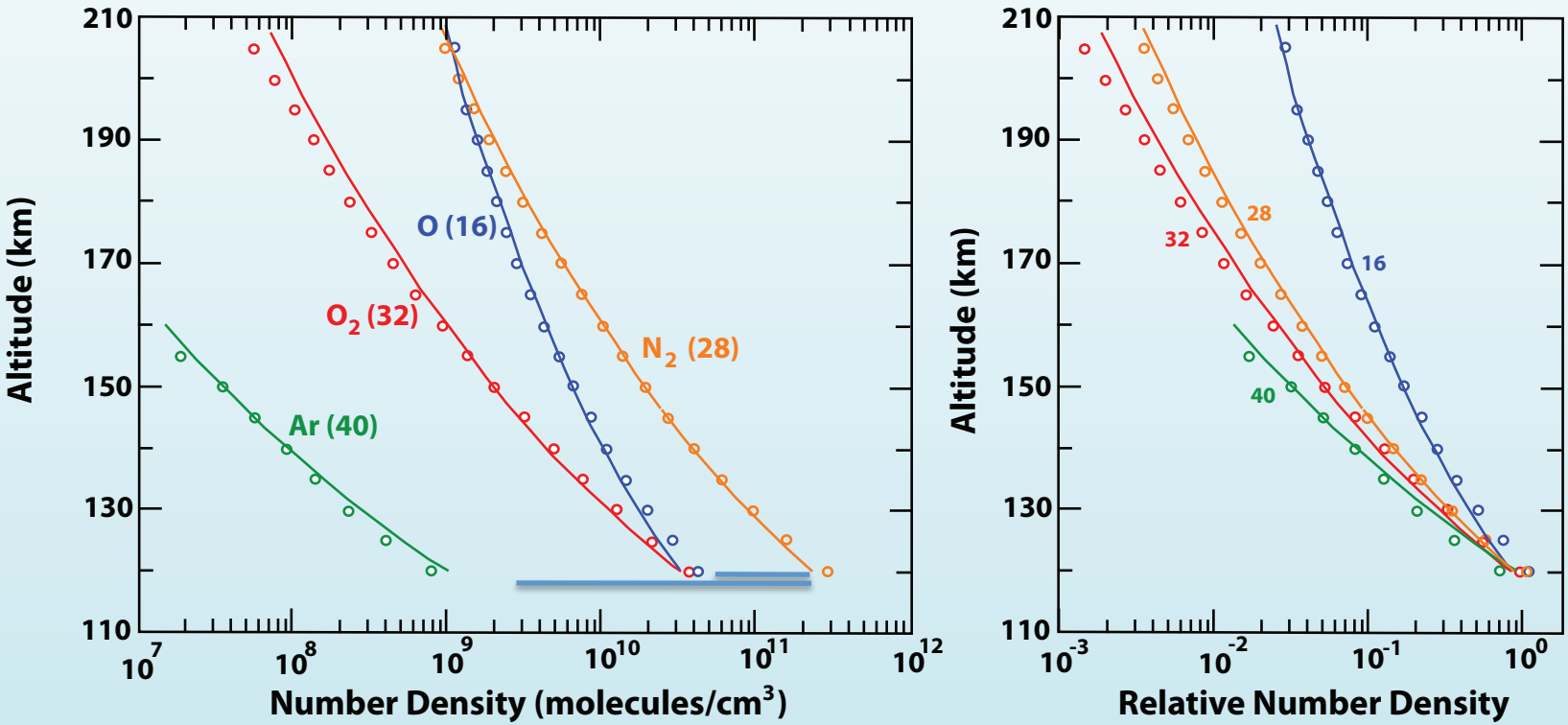
There were alternative theories

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.**

Question asked over and over when making presentations on fluorocarbon-ozone theory:

Fluorocarbons are heavier than air-how can they get to the stratosphere?



Diffusive Separation in the Thermosphere: a concept studied since the 1960s: graphs redrawn from Hedin and Nier (1965)

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.**

Quotes

- **Committee: A cul-de-sac to which ideas are lured and then quietly strangled. -- John A. Lincoln**

- **Man will occasionally stumble over the truth but most of the time he will pick himself up and continue on. -- W. S. Churchill**

- **Don't worry about people stealing your ideas. If your ideas are any good, you'll have to ram them down people's throats. – unknown**

- **A complex system that works is invariably found to have evolved from a simple system that worked ...A complex system designed from scratch never works and cannot be patched up to make it work. You have to start over, beginning with a working simple system. -- Grady Booch**