Stratospheric Ozone:
Evaluating Potential Ozone Depleting Substance Substitutes

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CSD/ESRL

How do we Evaluate Substitutes ?

- Laboratory Measurements
- Atmospheric Monitoring
- Modeling Studies
- Assessments

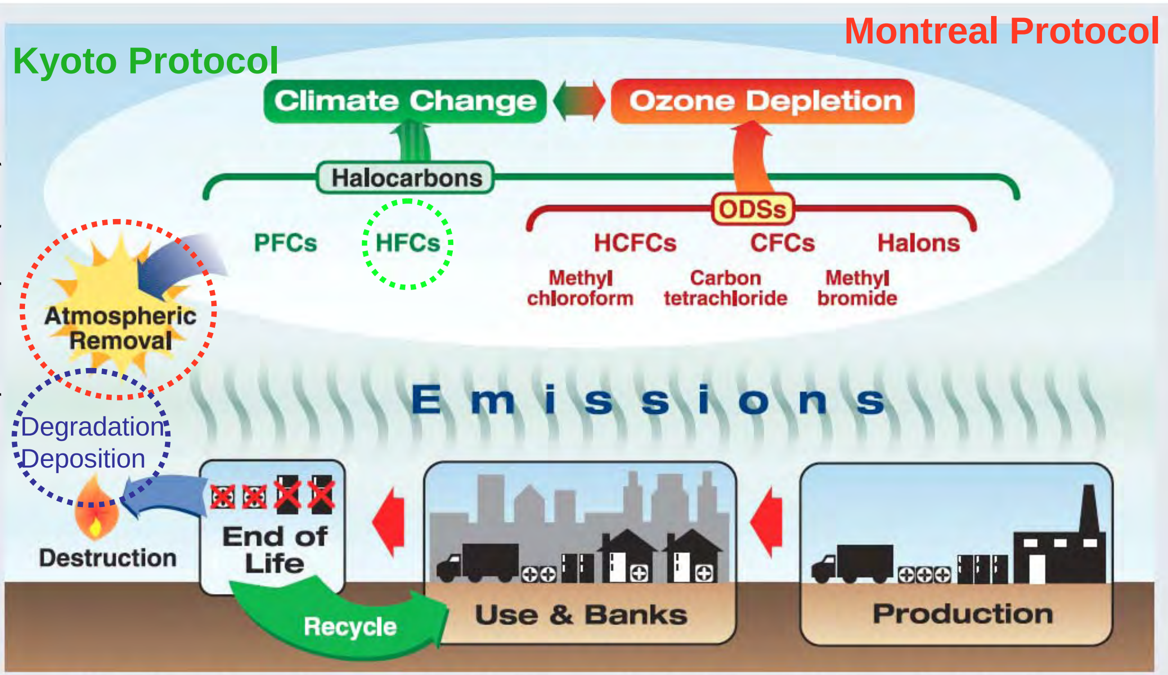
NOAA's Climate Goal

Performance Measure: Testing "climate and stratospheric ozone friendliness of proposed substitutes"

ESRL Atmospheric Chemistry Review
29-31 January 2008

Ozone Depleting Substance Substitutes

Evaluation of the environmental impact of a compound from production to end-of-life



Taken from IPCC Special Report (2005)

Proper Choice of Substitutes can lead to:
"Win - Win"
Climate - Ozone

Laboratory Studies are used to Evaluate and Quantify:

1. **Atmospheric Removal**
2. **Climate Impact**
3. **Degradation Products**

What is a Good Substitute ?

- ✓ Zero ODP
- ✓ Short Atm. Lifetime
- ✓ Low GWP
- ✓ Minimal Impact of Degradation Products

Climatic Impact of a Radiative Forcing Agent

Global Warming Potential (GWP)

Index used to compare forcing agents

$$GWP_X(T) = \frac{\int_0^T RF_X(t)\,dt}{\int_0^T RF_{CO2}(t)\,dt} = \frac{RE_X\,\tau\left[1 - e^{-\frac{T}{\tau}}\right]}{Int\ RF_{CO2}(T)}$$

Laboratory Measurements

Radiative Efficiency (RE)

Atmospheric Lifetime

ODS Substitute Evaluation

Kinetics

Infrared Spectroscopy

Photochemistry

Modeling

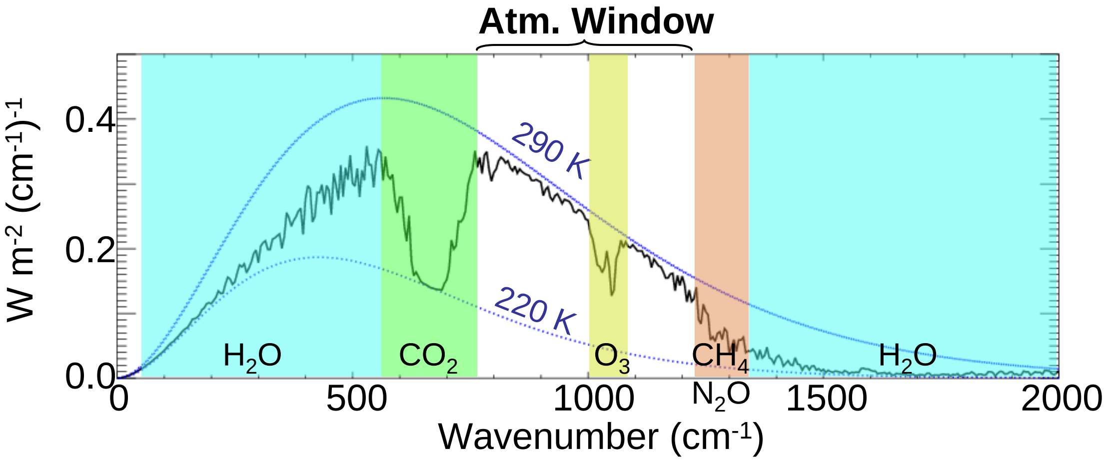
UV Spectroscopy

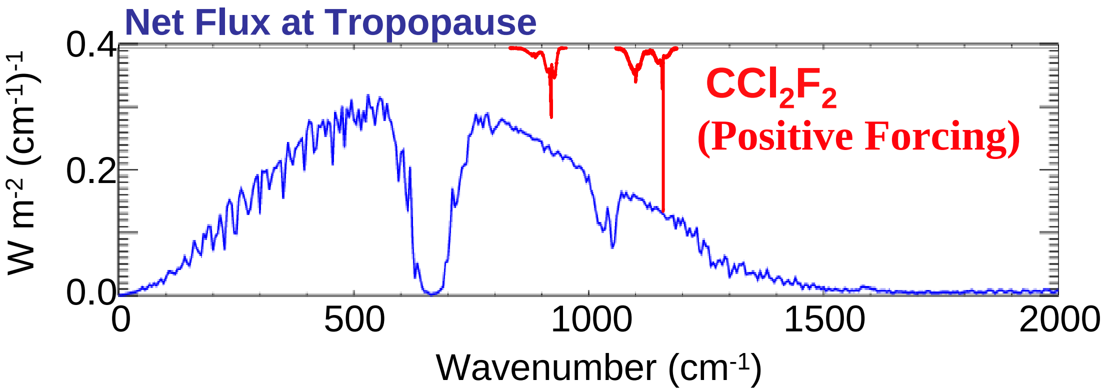
Climatic Impact of a Radiative Forcing Agent

Radiative Efficiency (RE)

How strongly a forcing agent affects the radiative balance at the tropopause

- **Infrared Spectrum**
- **Radiative Transfer Model**





Collaborations within CSD for model calculations:
This work by Bob Portmann

Climatic Impact of a Radiative Forcing Agent

Atmospheric Lifetime (τ)

How long the molecule persists in the atmosphere

$$\frac{1}{\tau} = \frac{1}{\tau_{Trop}} + \frac{1}{\tau_{Strat}} + \frac{1}{\tau_{Other}}$$

Loss Processes
- **Reaction: OH, Cl, O_3, NO_3, $O(^1D)$**
- **UV Photolysis**
- **Wet and Dry Deposition**

τ_{Strat} ⇨ Decades

Good Substitutes ⇨ Trop. Loss

Two Laboratory Measurement Case studies

1) $CF_3CF{=}CH_2$ and (Z)-$CF_3CF{=}CFH$ — HFC-134a
2) SO_2F_2 — CH_3Br

Case Study: $CF_3CF=CH_2$ and (Z)-$CF_3CF=CFH$

Hydrofluoro olefins (HFOs)

Reactive: Carbon Double Bond
GHGs: C-F stretch

- **Potential Substitutes for HFC-134a**

  Mobile Air Conditioning units

  EU directive:

  Replacement (or Alternatives) by 2011

  Phase-out by 2015

HFC-134a (CF_3CFH_2)	
Lifetime	14 years
ODP	0
GWP	~1400

- **Response to Kyoto Protocol**

▪ ***DuPont proposed (Z)-$CF_3CF=CFH$***

▪ ***CSD evaluated via laboratory measurements (DuPont provided (Z)-$CF_3CF=CFH$ sample)***

Laboratory Measurements

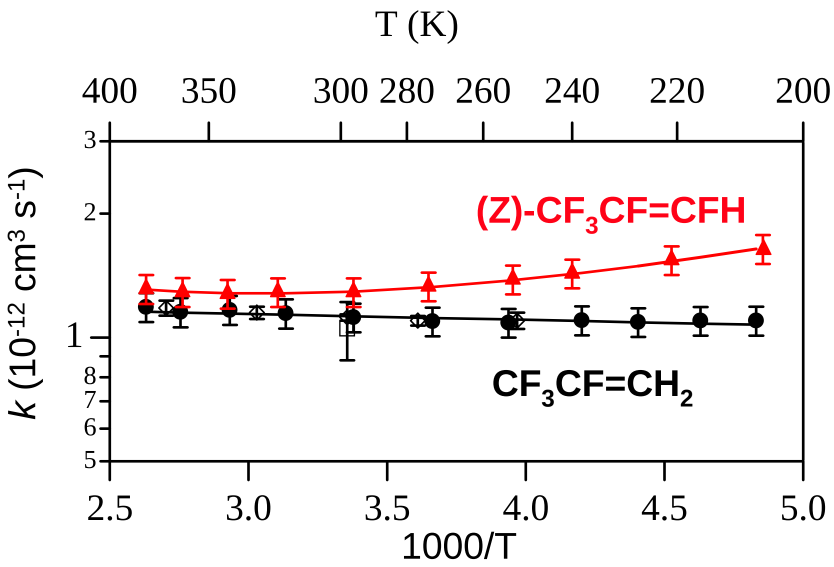
(1) OH + HFOs → Products

Pulsed Laser Photolysis -
Laser Induced Fluorescence Method

Non-Arrhenius behavior
Pressure Independent

$\tau_{OH} \sim 10$ Days

$[OH]_{Atm}$ = 1 x 10^6 cm^{-3}
Lifetime dependent on season and location



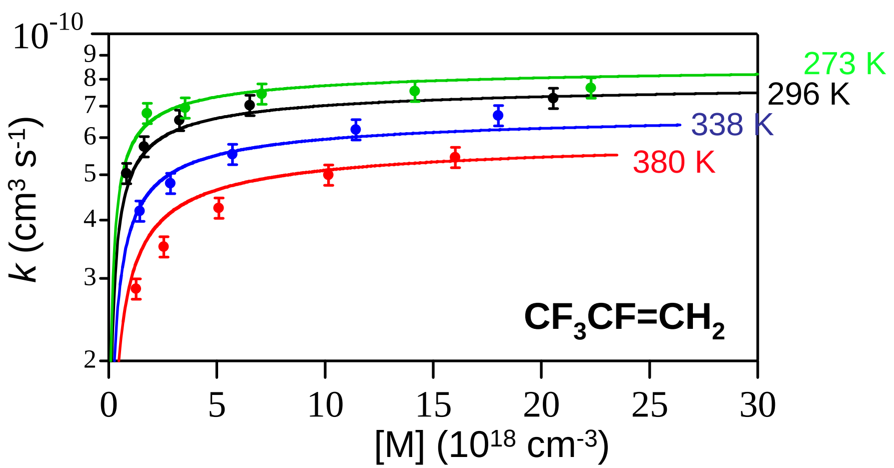
(2) Cl + HFOs + M → Products

Relative Rate Method

Very Fast (70 x k_{OH})
Pressure Dependent

$\tau_{Cl} \sim 16$ Days

$[Cl]_{Atm}$ = 1 x 10^4 cm^{-3}
Uncertainties in $[Cl]_{Atm}$



(3) UV Photolysis

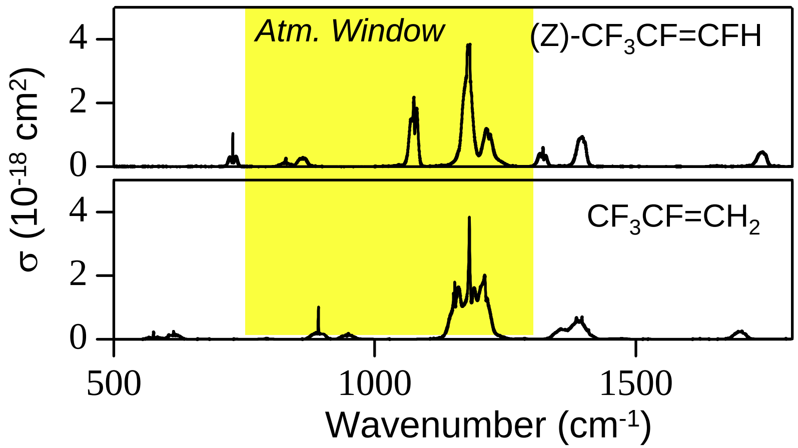
$\tau_{UV} > 300$ yrs

$\tau_{O_3} > 12$ yrs

Nielsen et al. (2007), $CF_3CF=CH_2$

HFO Case Study

✓ **Radiative Efficiency (RE)**

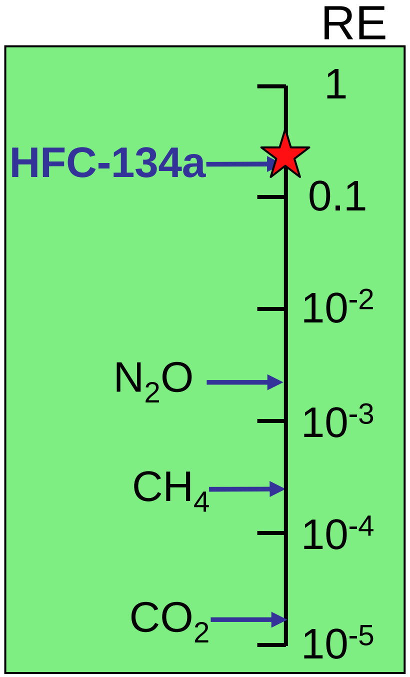


0.26 W m^{-2} ppb^{-1}

0.24 W m^{-2} ppb^{-1}

(Strong IR absorber)

Line-by-line Radiative Transfer Model



✓ **Atmospheric Lifetime (τ)**

OH and Cl Reaction

< 10 Days

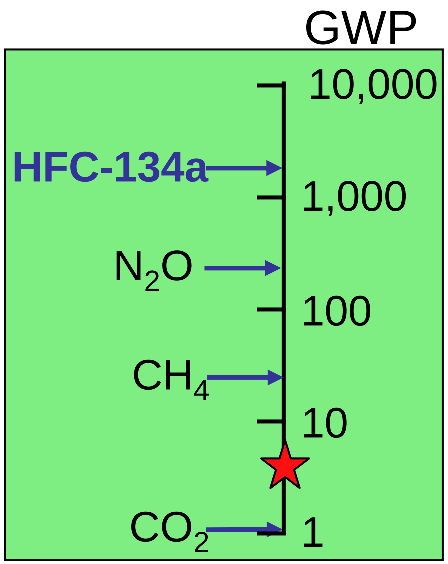
(Short-Lived)

✓ **Global Warming Potential (GWP)**

Not well-mixed globally

< 5

100 yr Time Horizon



HFO Case Study

Reaction Products and Yields Measured

- *Some Products are also GHGs*
- *Short atmospheric lifetimes (<10 days)*
- *Environmentally persistent products*
- *Products with ODP (Cl degradation)*

CF_3CFO (100% Yield) → $CF_3C(O)OH$ (TFA)

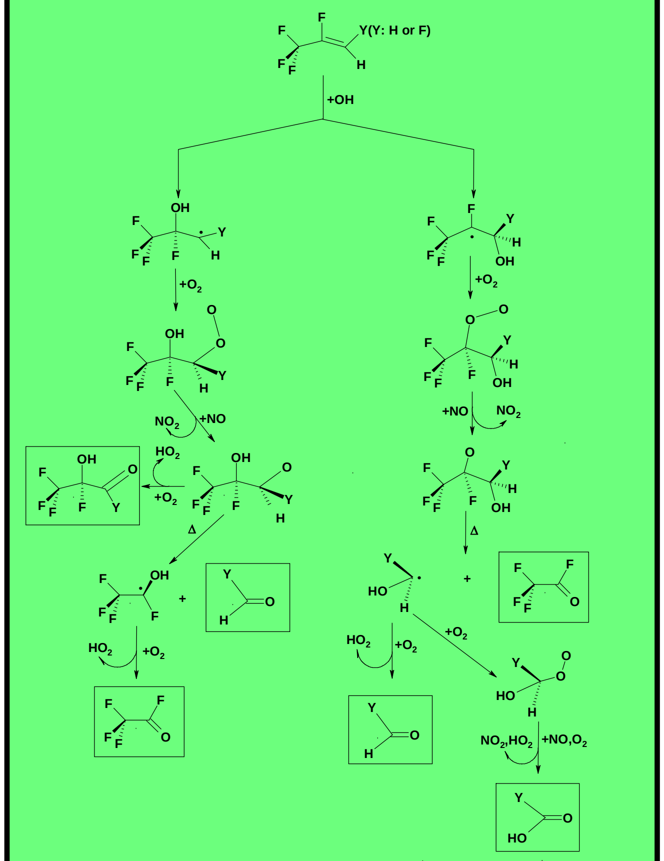
Environmentally persistent pollutant
Health Effects (toxin)

HFC-134a: 10% CF_3CFO Yield

HClCO → $CF_3CF{=}CH_2$ ~50% Yield
$CF_3CF{=}CFH$ 0 Yield

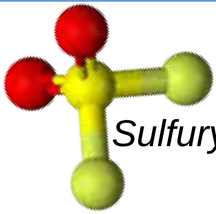
Small but non-zero ODP

Atmospheric Degradation Mechanism



Win	-	Win	-	?
Ozone	-	Climate	-	Ecosystem

SO_2F_2 Case Study



Substitute for CH_3Br

	CH_3Br
Lifetime	~ 0.7 years
ODP	0.6
GWP	5

Fumigant: Biocide (toxic)
In use commercially

Recently Discovered in the Atmosphere (~ 1 ppt)

Mühle et al. AGU 2006
Scripps Inst. Oceanography

Atmospheric Degradation/Lifetime Uncertain !

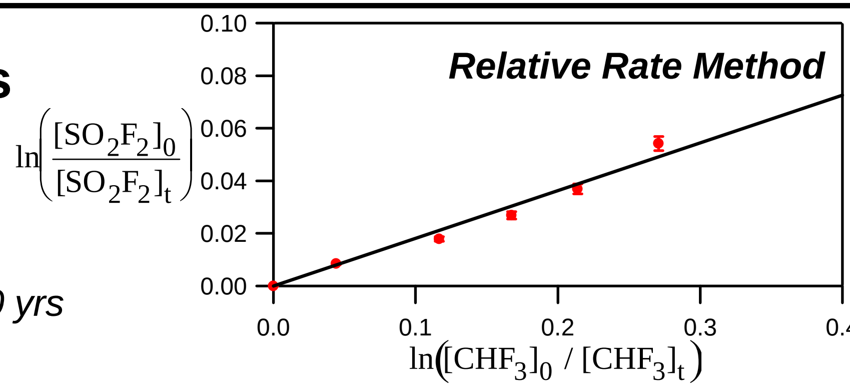
Laboratory Measurements

(1) OH + $SO_2F_2 \rightarrow$ Products

$$\tau_{OH} > 300 \text{ yrs}$$

** previous estimate > 30 yrs*

$[OH]_{Atm} = 1 \times 10^{6}$ cm^{-3}



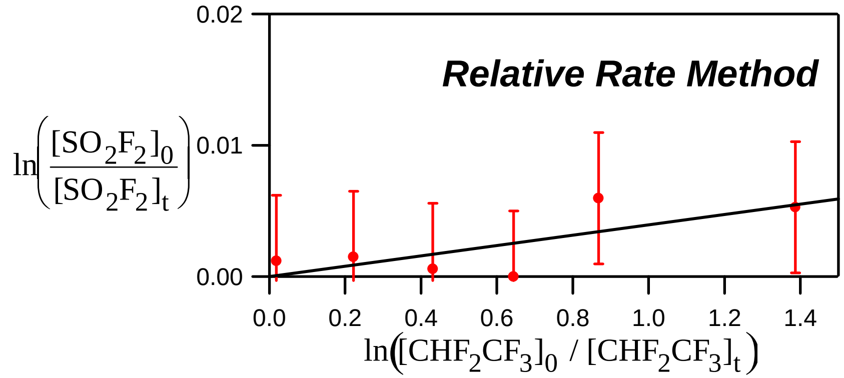
T = 296 K

$k < 1 \times 10^{-16}$
cm^3 $molecule^{-1}$ s^{-1}

(2) Cl + $SO_2F_2 \rightarrow$ Products

$$\tau_{Cl} > 30,000 \text{ yrs}$$

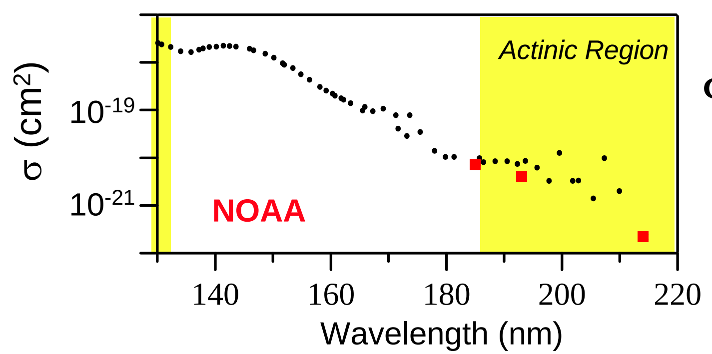
$[Cl]_{Atm} = 1 \times 10^{4}$ cm^{-3}



$k < 5 \times 10^{-17}$
cm^3 $molecule^{-1}$ s^{-1}

(3) UV Photolysis

$$\tau_{UV} > 4,000 \text{ yrs}$$



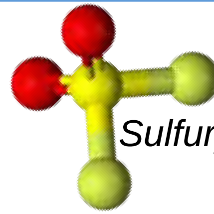
Φ < 0.03 @ 193 nm

$\tau_{O(^1D)} = 700$ yrs
Dillon et al. (2007)

$\tau_{O_3} > 24,000$ yrs
Dillon et al. (2007)

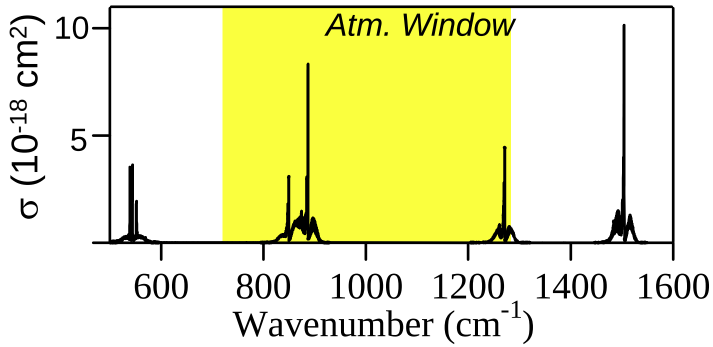
$\tau_{\text{Ocean Uptake}} = 20 - 40$ yrs
Mühle et al. (Scripps)

SO_2F_2 Case Study



Sulfuryl fluoride

✓ **Radiative Efficiency (RE)**



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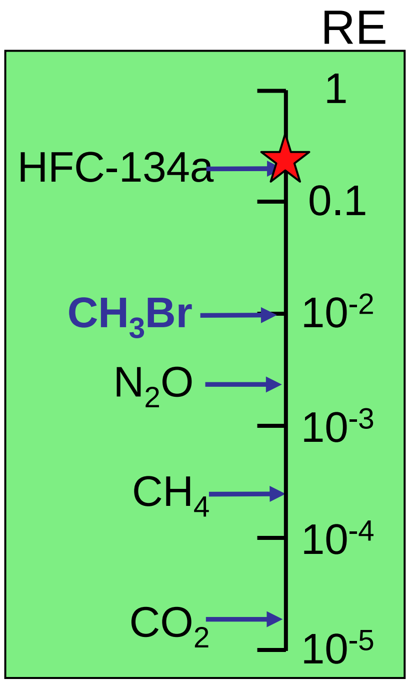
Line-by-line Radiative Transfer Model



✓ **Atmospheric Lifetime**

Ocean Uptake

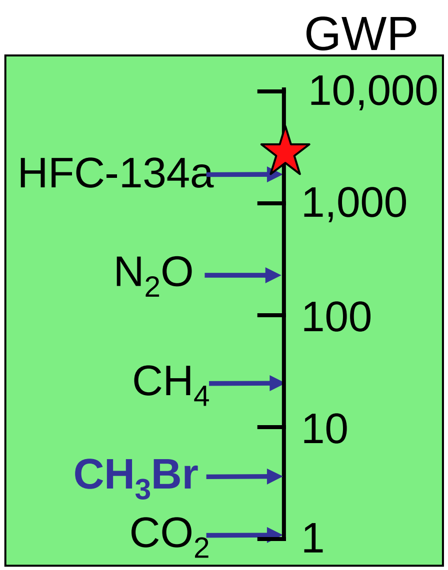
20 - 40 Yrs

(Long-Lived)

✓ **Global Warming Potential (GWP)**

~ 4000 ± 1500

100 yr Time Horizon

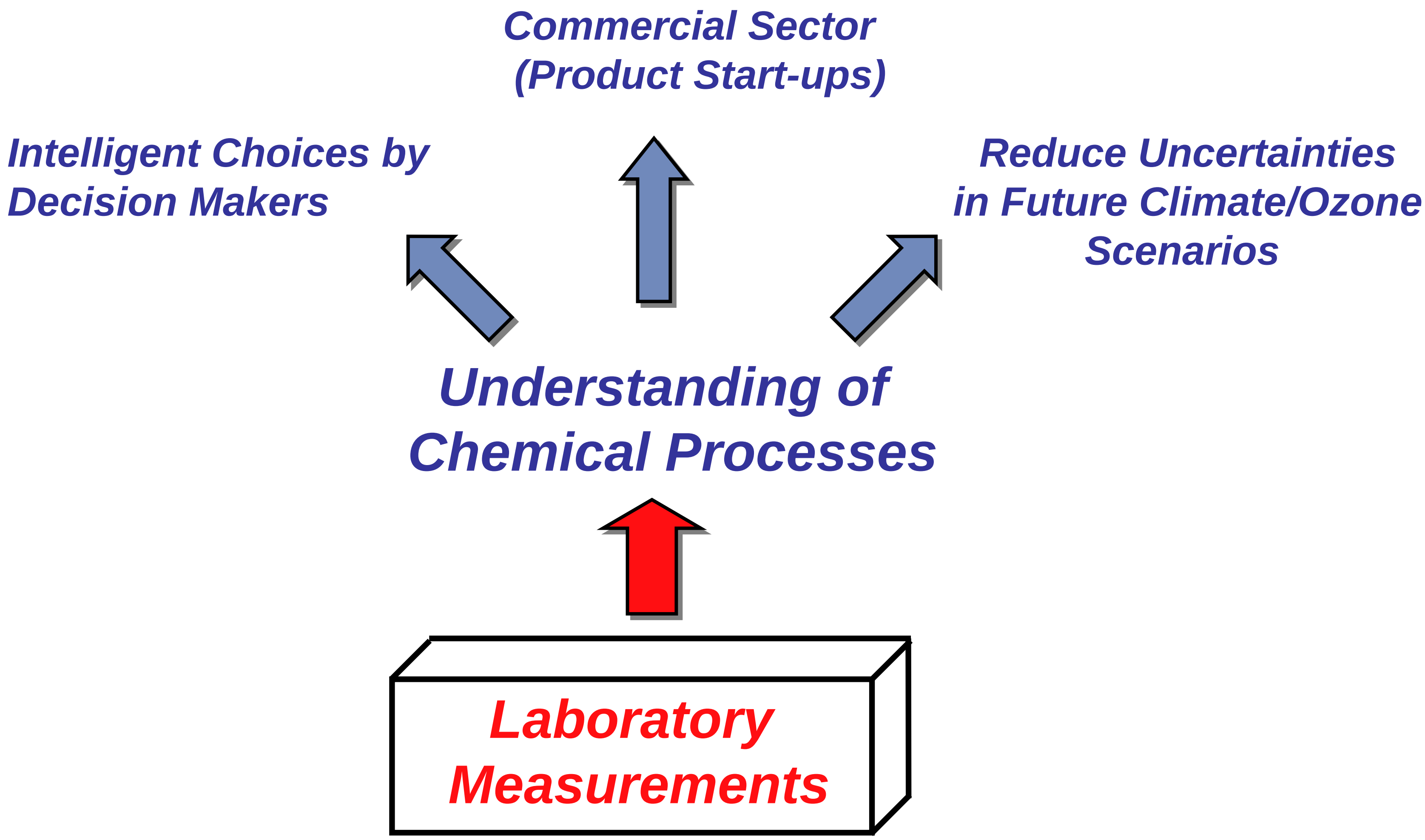


Win - Lose

Ozone - Climate

NOAA's Climate Goal

"Understand Climate Variability and Change to Enhance Society's Ability to Plan and Respond"



Further examples of Lab Studies in Talks and during CSD Lab Tour