The Impact of Laboratory Photochemistry on the Montreal Protocol

James B. Burkholder

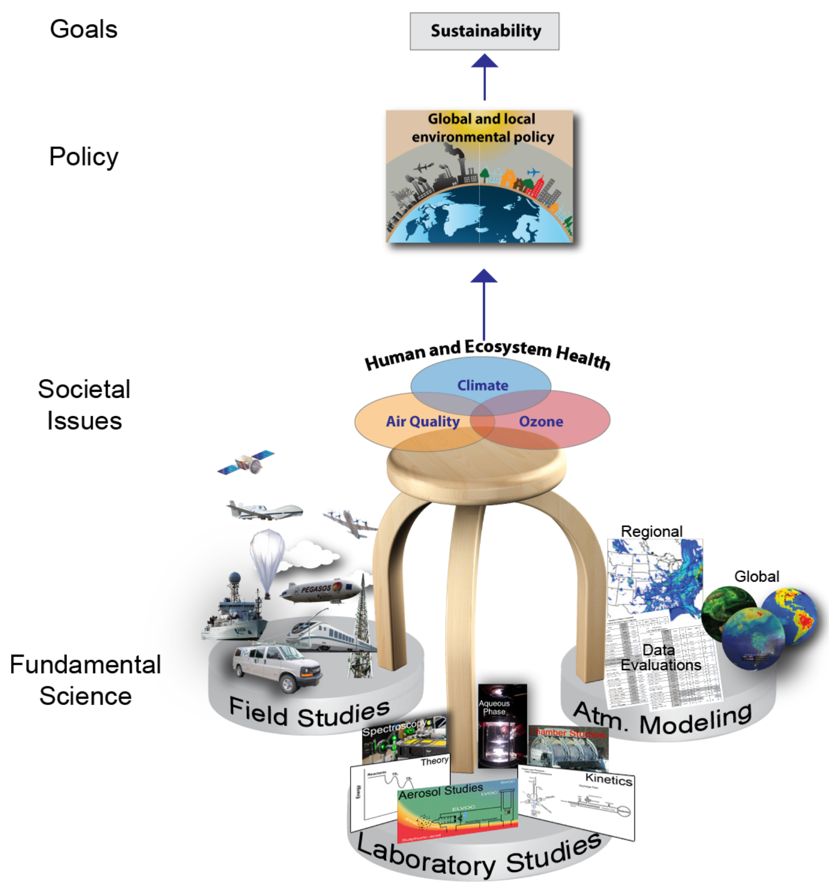
Earth System Research Laboratory
Chemical Sciences Division
National Oceanic and Atmospheric Administration (NOAA)
Boulder, CO
USA

What is "Laboratory Photochemistry" ?

The study of elementary chemical processes under controlled conditions (*relevant to the atmosphere*)

Reaction Rate Constants (OH, $O(^1D)$, Cl, …)
UV Photolysis Rates
Reaction Mechanisms
Infrared Spectra

How is it Relevant to the Montreal Protocol ?



Annex A, B, C, and F Compounds

CFCs, Halons, HCFCs, HBFCs, and HFCs

Replacement Compounds: HFOs

"The three-legged stool"

Building Blocks
Honest Brokers of Information

Burkholder et al.
"The Essential Role for Laboratory Studies in Atmospheric Chemistry"
Environ. Sci. & Tech., 2017, 51, 2519-2528

Laboratory Studies → Modeling → Improved Understanding → Informed Policy

Policy Relevant Metrics

Atmospheric Lifetime
Radiative Efficiency (RE)

Ozone Depletion Potential (ODP)
Global Warming Potential (GWP)

Metric

Lifetime (τ)

$$\frac{1}{\tau} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{O(^1D)}} + \frac{1}{\tau_{UV}} + \ldots$$

Ozone Depletion Potential (ODP)

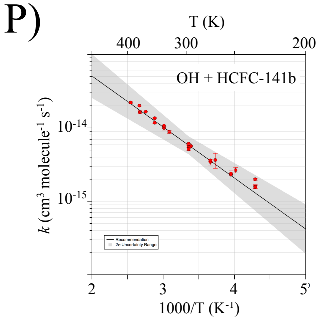
$$\mathrm{ODP}_i = \frac{n_{\mathrm{Cl}}}{3}\,\frac{f_i}{f_{\mathrm{CFC-11}}}\,\frac{\mathrm{M}_{\mathrm{CFC-11}}}{\mathrm{M_i}}\,\frac{\tau_i}{\tau_{\mathrm{CFC-11}}}$$

Global Warming Potential (GWP)

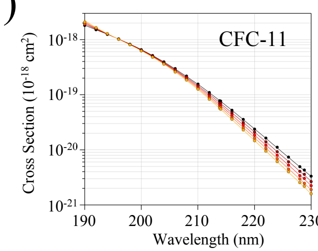
$$\mathrm{GWP(T)} = \frac{RE(\tau)\,\tau\,[1-\exp(-\mathrm{T}/\tau)]}{\mathrm{M_i}\,Int\,RF_{\mathrm{CO_2}}(\mathrm{T})}$$

Laboratory Measurement

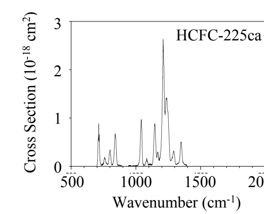
Reaction Rate Coefficients (T, P)
OH radical, $O(^1D)$, Cl-atom



UV Absorption Spectrum (λ,T)



Infrared Absorption Spectrum



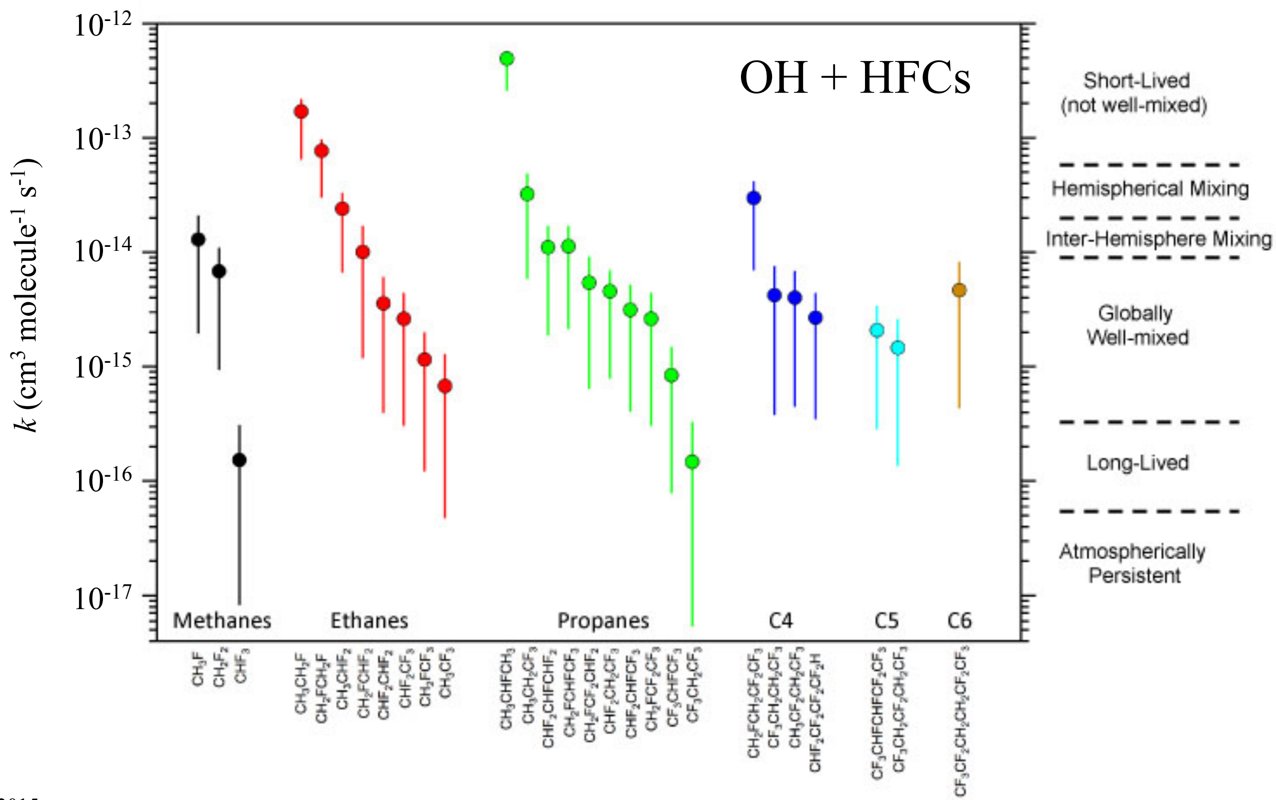
CFCs, Halons, HCFCs, HBFCs, and HFCs (Annex A,B,C, and F)
Replacement Compounds: HFOs

Why Study Individual Compounds in the Laboratory?

Composition and structure of a molecule influences its reactivity and photolysis (*lifetime*)

OH Reaction Rate Coefficients

Mixing | **Lifetime**



Days

6 Months

Years

50 Years

500 Years

Burkholder et al., Chem. Rev., 2015
"Atmospheric degradation of ozone depleting substances, their substitutes, and related species"

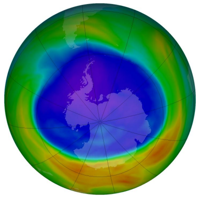
ClO Dimer

Data Evaluation

Proposed Replacements

HCFC GWPs

ClO Dimer (Cl_2O_2)



Catalytic Ozone Destruction Cycle

Molina and Molina (1987)

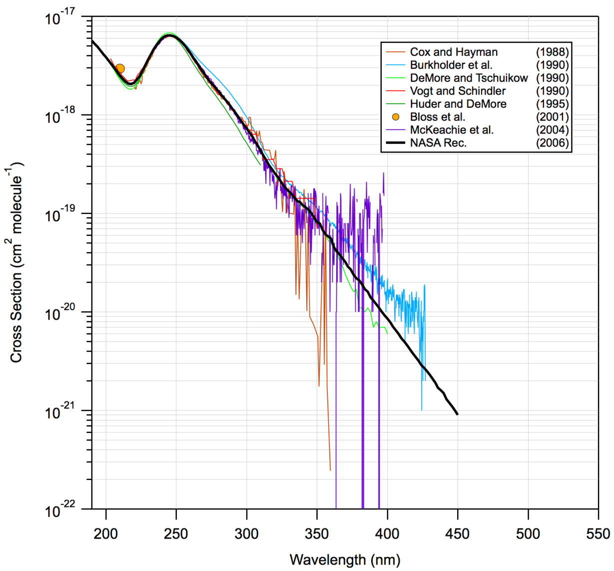
$$\mathbf{Cl} + O_3 \rightarrow ClO + O_2$$
$$ClO + ClO + M \rightarrow Cl_2O_2 + M$$
$$\color{red}{Cl_2O_2 + h\nu \rightarrow \mathbf{Cl} + ClOO}$$
$$ClOO \rightarrow \mathbf{Cl} + O_2$$

Net: $2O_3 + h\nu \rightarrow 3O_2$

Cl_2O_2 photolysis rate is the key step for ozone depletion

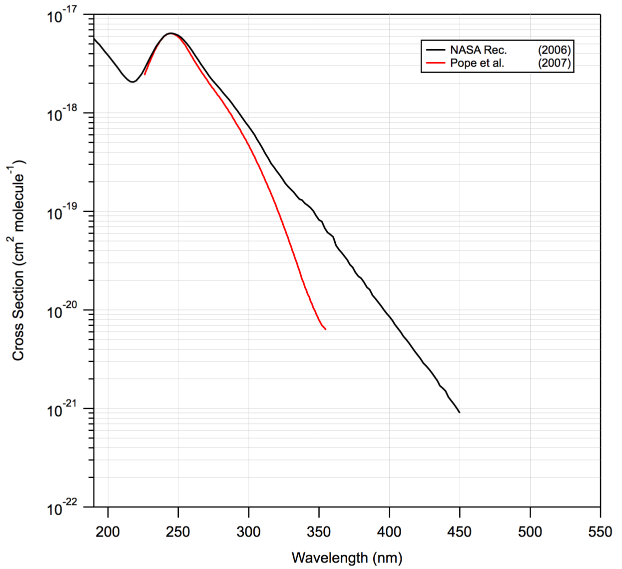
$$J = \int \color{red}{\boldsymbol{\sigma}(\boldsymbol{\lambda}, \boldsymbol{T})}\, \phi(\lambda)\, F(\lambda, Z, SZA)\, d\lambda$$

Pre-2007 Studies and NASA (2006) Recommendation



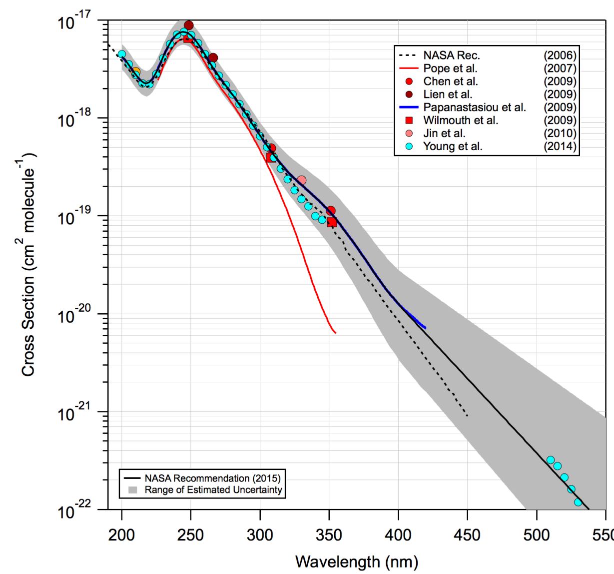
Lab studies confirm importance of ClO dimer cycle

Pope et al. (2007) and NASA (2006) Recommendation



Pope et al. challenges understanding of polar ozone depletion chemistry

Post 2007 Studies and NASA (2015) Recommendation



Labs responded, improve dataset, resolve discrepancy

ClO Dimer

Data Evaluation

Proposed Replacements

HCFC GWPs

Data Evaluation

JPL Publication **15-10**

Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies

Evaluation Number 18

NASA Panel for Data Evaluation:

J. B. Burkholder
Earth System Research Laboratory
National Oceanic and Atmospheric Administration (NOAA)

S. P. Sander
Jet Propulsion Laboratory
California Institute of Technology

J. P. D. Abbatt
University of Toronto

J. R. Barker
University of Michigan

R. E. Huie
National Institute of Standards and Technology

C. E. Kolb
Aerodyne Research, Inc.

M. J. Kurylo
Goddard Earth Sciences, Technology and Research Program

V. L. Orkin
National Institute of Standards and Technology

D. M. Wilmouth
Harvard University

P. H. Wine
Georgia Institute of Technology

National Aeronautics and Space Administration

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

October, 2015

Data evaluations play an important role in atmospheric chemistry research; since the 1970s.

Recommendations of photochemical parameters for use in atmospheric models and laboratory studies

NASA Data Evaluation includes:

8 CFCs	17 HCFCs
13 Halons	28 HFCs
	16 HFOs

Annex A: All Compounds

Annex B: CF_3Cl, CCl_4, and CH_3CCl_3 (*34*)

Annex C, *Group I*: 8 ** and 9 others (*274*)

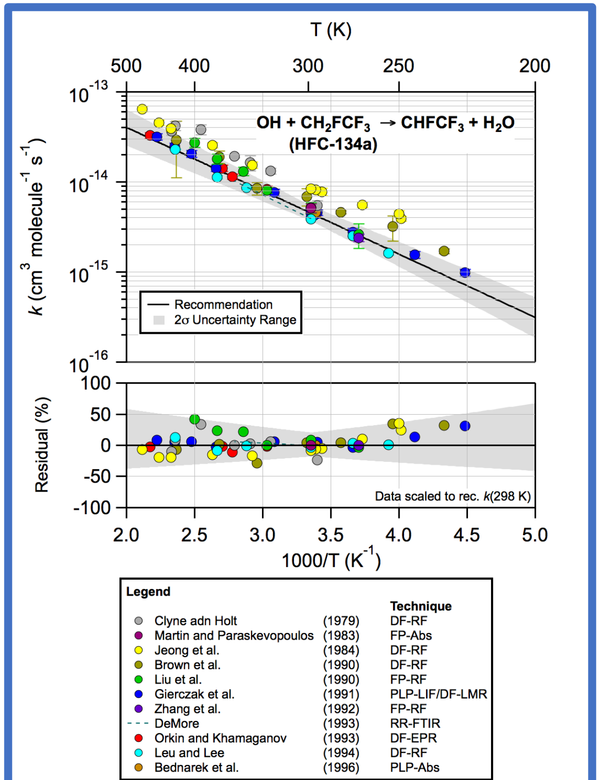
Group II: CHF_2Br and CF_3CHFBr (*274*)

Group III: CH_2BrCl (*1*)

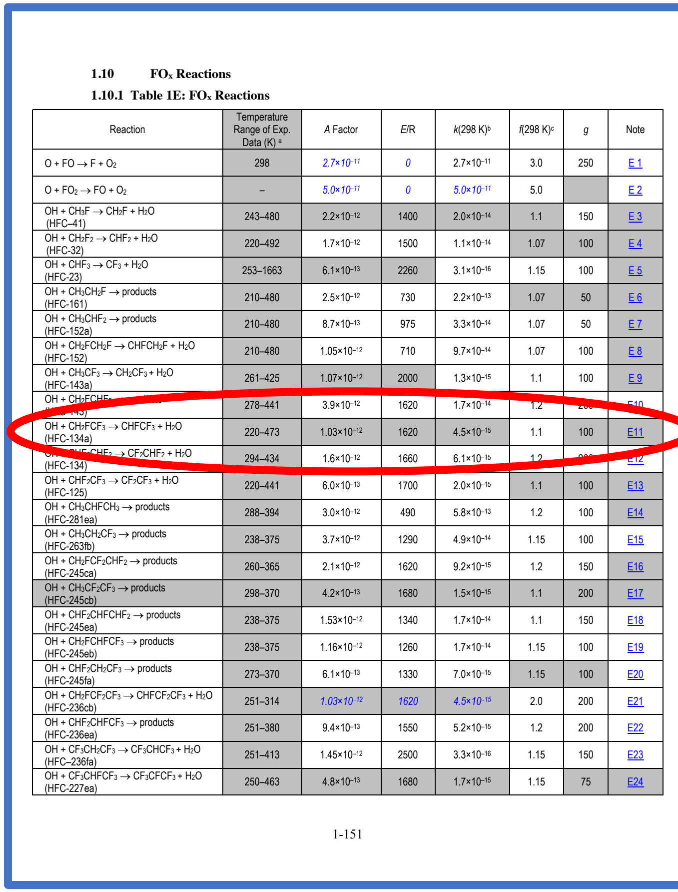
Annex F: All Compounds

Data Evaluation

Laboratory Studies



Recommendation



1.10 FO_x Reactions

1.10.1 Table 1E: FO_x Reactions

Reaction	Temperature Range of Exp. Data (K) [a]	*A* Factor	*E*/R	*k*(298 K)[b]	*f*(298 K)[c]	*g*	Note
O + FO → F + O_2	298	2.7×10^{-11}	0	2.7×10^{-11}	3.0	250	E 1
O + FO_2 → FO + O_2	–	5.0×10^{-11}	0	5.0×10^{-11}	5.0		E 2
OH + CH_3F → CH_2F + H_2O (HFC–41)	243–480	2.2×10^{-12}	1400	2.0×10^{-14}	1.1	150	E 3
OH + CH_2F_2 → CHF_2 + H_2O (HFC-32)	220–492	1.7×10^{-12}	1500	1.1×10^{-14}	1.07	100	E 4
OH + CHF_3 → CF_3 + H_2O (HFC-23)	253–1663	6.1×10^{-13}	2260	3.1×10^{-16}	1.15	100	E 5
OH + CH_3CH_2F → products (HFC-161)	210–480	2.5×10^{-12}	730	2.2×10^{-13}	1.07	50	E 6
OH + CH_3CHF_2 → products (HFC-152a)	210–480	8.7×10^{-13}	975	3.3×10^{-14}	1.07	50	E 7
OH + CH_2FCH_2F → $CHFCH_2F$ + H_2O (HFC-152)	210–480	1.05×10^{-12}	710	9.7×10^{-14}	1.07	100	E 8
OH + CH_3CF_3 → CH_2CF_3 + H_2O (HFC-143a)	261–425	1.07×10^{-12}	2000	1.3×10^{-15}	1.1	100	E 9
OH + CH₂FCHF [illegible]	278–441	3.9×10^{-12}	1620	1.7×10^{-14}	1.2	[illegible]	E10
OH + CH_2FCF_3 → $CHFCF_3$ + H_2O (HFC-134a)	220–473	1.03×10^{-12}	1620	4.5×10^{-15}	1.1	100	E11
[illegible] → CF_2CHF_2 + H_2O (HFC-134)	294–434	1.6×10^{-12}	1660	6.1×10^{-15}	1.2	[illegible]	E12
OH + CHF_2CF_3 → CF_2CF_3 + H_2O (HFC-125)	220–441	6.0×10^{-13}	1700	2.0×10^{-15}	1.1	100	E13
OH + CH_3CHFCH_3 → products (HFC-281ea)	288–394	3.0×10^{-12}	490	5.8×10^{-13}	1.2	100	E14
OH + $CH_3CH_2CF_3$ → products (HFC-263fb)	238–375	3.7×10^{-12}	1290	4.9×10^{-14}	1.15	100	E15
OH + $CH_2FCF_2CHF_2$ → products (HFC-245ca)	260–365	2.1×10^{-12}	1620	9.2×10^{-15}	1.2	150	E16
OH + $CH_3CF_2CF_3$ → products (HFC-245cb)	298–370	4.2×10^{-13}	1680	1.5×10^{-15}	1.1	200	E17
OH + $CHF_2CHFCHF_2$ → products (HFC-245ea)	238–375	1.53×10^{-12}	1340	1.7×10^{-14}	1.1	150	E18
OH + $CH_2FCHFCF_3$ → products (HFC-245eb)	238–375	1.16×10^{-12}	1260	1.7×10^{-14}	1.15	100	E19
OH + $CHF_2CH_2CF_3$ → products (HFC-245fa)	273–370	6.1×10^{-13}	1330	7.0×10^{-15}	1.15	100	E20
OH + $CH_2FCF_2CF_3$ → $CHFCF_2CF_3$ + H_2O (HFC-236cb)	251–314	1.03×10^{-12}	1620	4.5×10^{-15}	2.0	200	E21
OH + CHF_2CHFCF_3 → products (HFC-236ea)	251–380	9.4×10^{-13}	1550	5.2×10^{-15}	1.2	200	E22
OH + $CF_3CH_2CF_3$ → CF_3CHCF_3 + H_2O (HFC–236fa)	251–413	1.45×10^{-12}	2500	3.3×10^{-16}	1.15	150	E23
OH + CF_3CHFCF_3 → CF_3CFCF_3 + H_2O (HFC-227ea)	250–463	4.8×10^{-13}	1680	1.7×10^{-15}	1.15	75	E24

1-151

Atmospheric Lifetime

13.4 years ± 14%

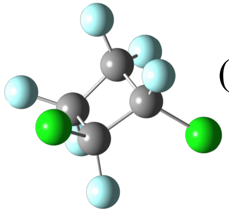
Uncertainty in laboratory measurements contributes to overall metric uncertainty

ClO Dimer

Data Evaluation

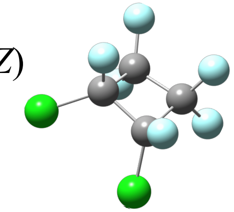
Proposed Replacements

HCFC GWPs



(*E*)

Proposed Replacements



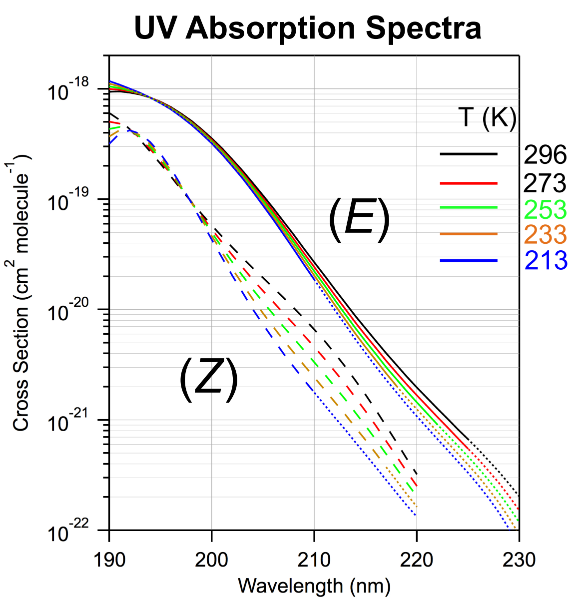
(*Z*)

R-316c, 1,2-$C_4Cl_2F_6$ (*E*,*Z*) CFC

NOAA Laboratory Studies

* Negligible OH reactivity

* $k(O(^1D)) = 1.6 \times 10^{-10}\ cm^3\ s^{-1}$
  Reactive yield = 0.88 ± 0.02



* 100% Photodissociation (@ 193 nm)

* c-C_4F_6
  Photolysis and reaction product

Isomers have different UV absorption spectra

Photolysis is primary loss process

Removed in the Stratosphere

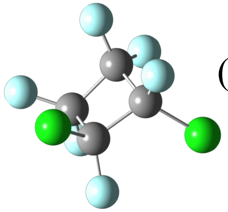
2-D model calculations (NASA/Goddard)

	(*E*)	(*Z*)
Lifetime (years)	75	114
ODP	0.45	0.54

Long-lived ODSs

Papadimitriou et al.
J. Phys. Chem. A (2013)

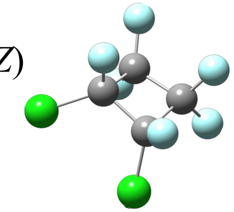
Proposed Replacements



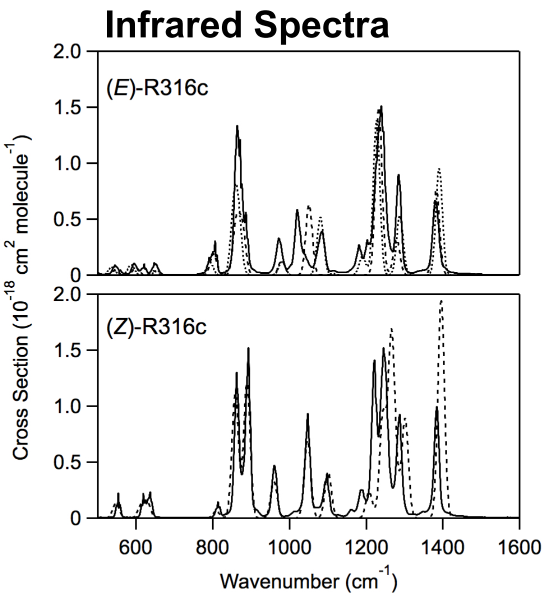
(*E*)

R-316c, 1,2-$C_4Cl_2F_6$ (*E*,*Z*) CFC

(*Z*)



NOAA Laboratory Studies



	(*E*)	(*Z*)
GWP_{100}	4160	5400

Potent Greenhouse Gases

Removed from consideration

Timely laboratory studies provide industry and policy relevant information

Papadimitriou et al.
J. Phys. Chem. A (2013)

ClO Dimer

Data Evaluation

Proposed Replacements

HCFC GWPs

Kigali Amendment to the Montreal Protocol

Annex C: Controlled Substances

GWPs for HCFCs

Group	Substance	Number of isomers	Ozone-Depleting Potential*	100-Year Global Warming Potential***
Group I				
$CHFCl_2$	HCFC-21**	1	0.04	151
CHF_2Cl	HCFC-22**	1	0.055	1810
CH_2FCl	HCFC-31	1	0.02	
C_2HFCl_4	HCFC-121	2	0.01–0.04	
$C_2HF_2Cl_3$	HCFC-122	3	0.02–0.08	
$C_2HF_3Cl_2$	HCFC-123	3	0.02–0.06	
$CHCl_2CF_3$	HCFC-123**	–	0.02	77
C_2HF_4Cl	HCFC-124	2	0.02–0.04	
$CHFClCF_3$	HCFC-124**	–	0.022	609
$C_2H_2FCl_3$	HCFC-131	3	0.007–0.05	
$C_2H_2F_2Cl_2$	HCFC-132	4	0.008–0.05	
$C_2H_2F_3Cl$	HCFC-133	3	0.02–0.06	
$C_2H_3FCl_2$	HCFC-141	3	0.005–0.07	
CH_3CFCl_2	HCFC-141b**	–	0.11	725
$C_2H_3F_2Cl$	HCFC-142	3	0.008–0.07	
CH_3CF_2Cl	HCFC-142b**	–	0.065	2310
C_2H_4FCl	HCFC-151	2	0.003–0.005	
C_3HFCl_6	HCFC-221	5	0.015–0.07	
$C_3HF_2Cl_5$	HCFC-222	9	0.01–0.09	
$C_3HF_3Cl_4$	HCFC-223	12	0.01–0.08	
$C_3HF_4Cl_3$	HCFC-224	12	0.01–0.09	
$C_3HF_5Cl_2$	HCFC-225	9	0.02–0.07	
$CF_3CF_2CHCl_2$	HCFC-225ca**	–	0.025	122
CF_2ClCF_2CHClF	HCFC-225cb**	–	0.033	595
C_3HF_6Cl	HCFC-226	5	0.02–0.10	
$C_3H_2FCl_5$	HCFC-231	9	0.05–0.09	
$C_3H_2F_2Cl_4$	HCFC-232	16	0.008–0.10	
$C_3H_2F_3Cl_3$	HCFC-233	18	0.007–0.23	
$C_3H_2F_4Cl_2$	HCFC-234	16	0.01–0.28	
$C_3H_2F_5Cl$	HCFC-235	9	0.03–0.52	
$C_3H_3FCl_4$	HCFC-241	12	0.004–0.09	
$C_3H_3F_2Cl_3$	HCFC-242	18	0.005–0.13	
$C_3H_3F_3Cl_2$	HCFC-243	18	0.007–0.12	
$C_3H_3F_4Cl$	HCFC-244	12	0.009–0.14	
$C_3H_4FCl_3$	HCFC-251	12	0.001–0.01	
$C_3H_4F_2Cl_2$	HCFC-252	16	0.005–0.04	
$C_3H_4F_3Cl$	HCFC-253	12	0.003–0.03	
$C_3H_5FCl_2$	HCFC-261	9	0.002–0.02	
$C_3H_5F_2Cl$	HCFC-262	9	0.002–0.02	
C_3H_6FCl	HCFC-271	5	0.001–0.03	

274 Controlled HCFCs

Isomers are unique substances

8 HCFCs have GWPs derived from experimental laboratory measurements

Atmospheric reactivity (lifetime)

Infrared absorption spectrum (RE)

NOAA Study

Determine GWPs missing in Annex C

- Atmospheric Lifetimes
- Radiative Efficiencies (RE)
- Global Warming Potentials (GWPs)

Papanastasiou et al. (2017) (*in prep*)

NOAA Study

Reliable methods needed to estimate τ and GWP in the absence of experimental data

Atmospheric Lifetime (τ)

$$\frac{1}{\tau} = \frac{1}{\tau_{OH}} + \frac{1}{\tau_{O(^1D)}} + \frac{1}{\tau_{UV}}$$

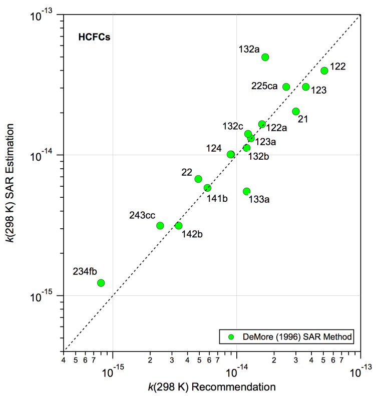
OH radical reaction

Predominant loss process for HCFCs

OH reaction rate coefficient

- Structure Activity Relationship (SAR): *DeMore (1996)*
  Estimated uncertainty: 20-30%
- Lifetime relative to CH_3CCl_3

$$\tau_{OH}^{HCFC} = \frac{k_{CH3CCl3}(272\text{ K})}{k_{HCFC}(272\text{ K})}\, \tau_{OH}^{CH3CCl3}$$



SAR works well

O(^{1}D) rate coefficient and lifetime

- Trends in reactivity: Baasandorj et al. (2013) (NOAA)
- Lifetimes: comparison with similar compounds, SPARC (2013)

UV photolysis lifetime

- Estimate based on HCFC chlorine content and distribution
- Comparison with 2-D model lifetimes: SPARC (2013)

NOAA Study

Reliable methods needed to estimate τ and GWP in the absence of experimental data

Global Warming Potential (GWP)

$$\mathrm{GWP(T)} = \frac{RE(\tau)\,\tau\,[1-\exp(-T/\tau)]}{M_i\ Int\ RF_{CO_2}(T)}$$

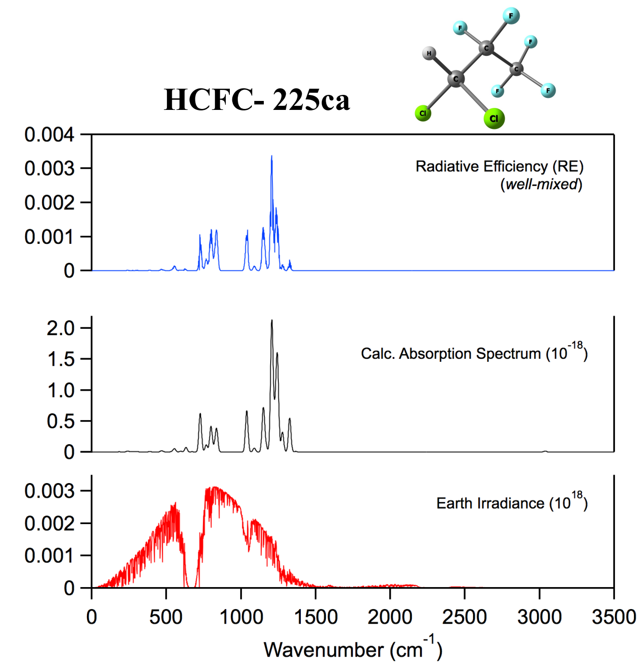
Estimating Infrared Absorption Spectra and RE

Theoretical methods used to calculate infrared absorption spectra

DFT: B3LYP/6-31G(2df,p); 50-100 hours CPU time per molecule

Empirical method used to calculate RE

Hodnebrog et al. (2013)



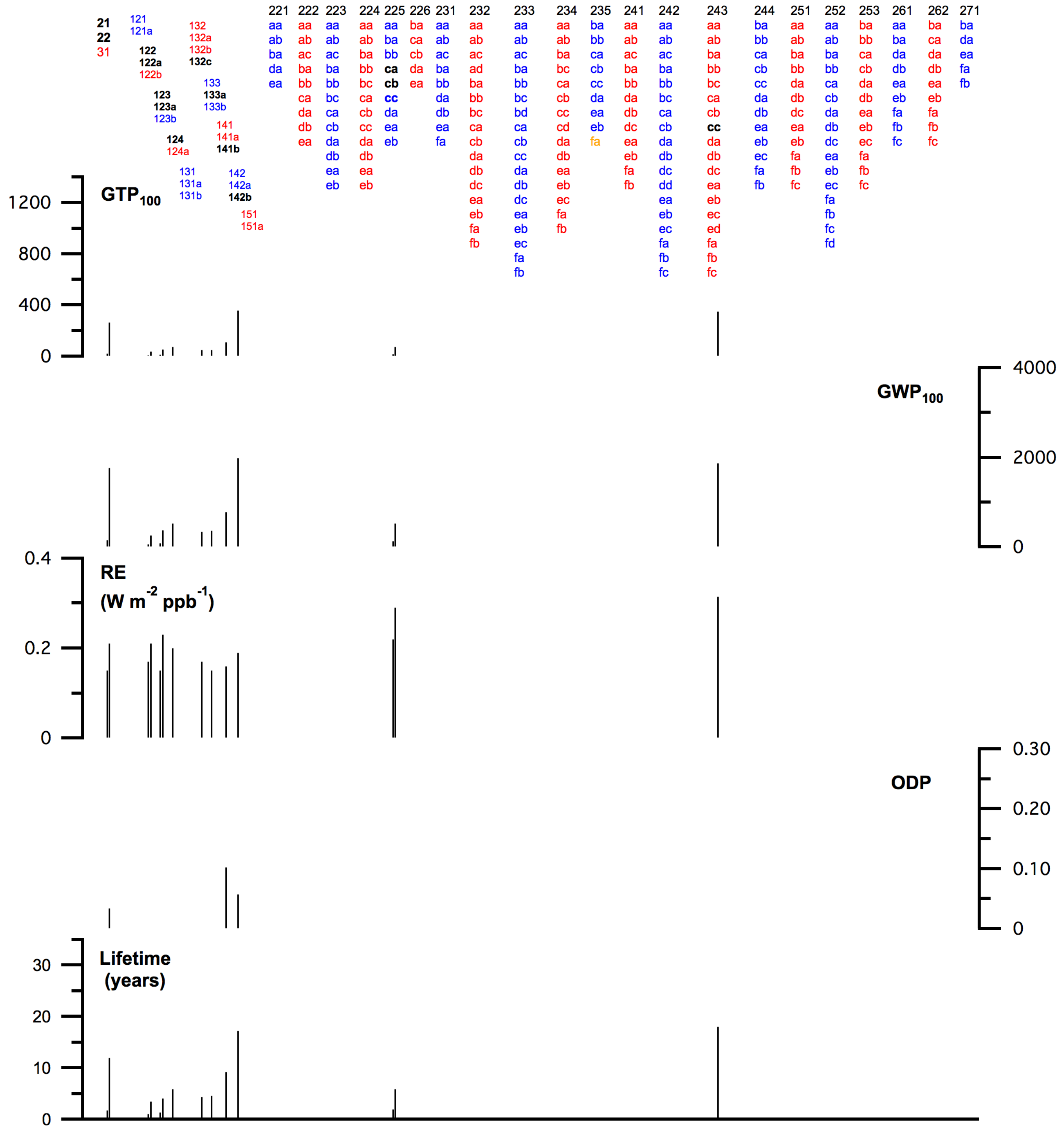
- Isomers have unique infrared absorption spectra
  Molecular geometry influences spectrum
- Strongest bands due to C-F stretches (~1000-1200 cm^{-1})
  Molecular geometry determines exact frequency
- Experimental spectra typically limited to >500 cm^{-1} region
  Theoretical calculations enable evaluation of low-frequency region

Good agreement between experimental and calculated spectra

Reliable RE determination (± ~15%)

Annex C HCFCs

Metrics available for only a few HCFCs



GTP

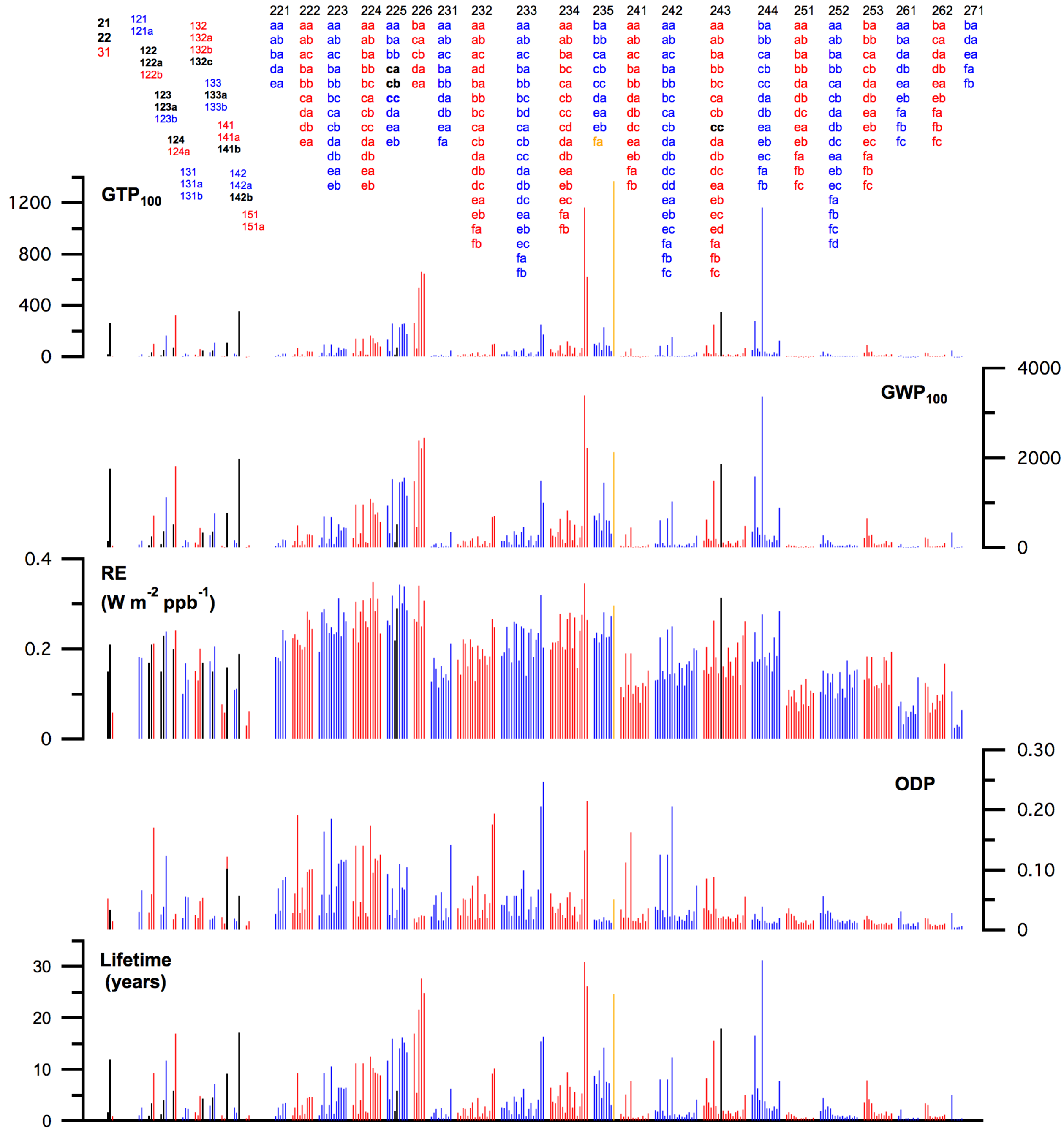
GWP

RE

ODP

Lifetime

Annex C HCFCs



GTP 1 – 3400

GWP 10 – 5400

** Isomeric dependence*

RE 0.03 – 0.35

ODP 33 >0.1

78 >0.05

Lifetime 0.3 – 60 years

** H-atom content*

** Isomeric form*

Large range in metric values !

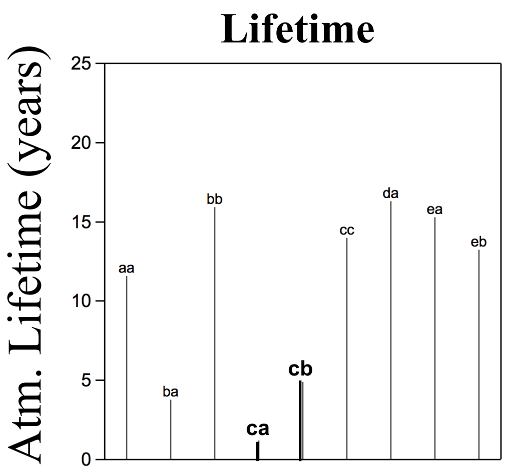
NOAA Study

Molecular geometry (*isomeric form*) influences OH reactivity (*lifetime*), RE, and GWP

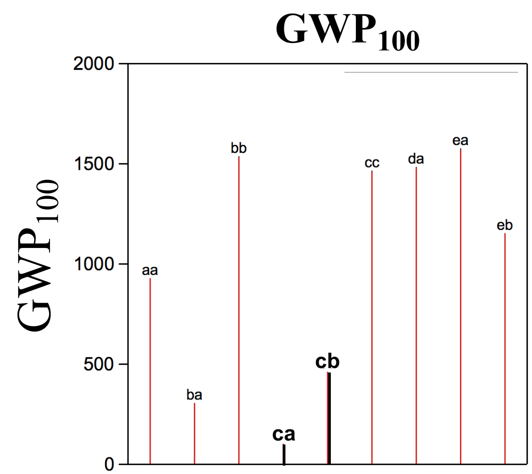
Consider on a molecule-by-molecule basis

HCFC-225 Isomers

aa	CHF_2-CCl_2-CF_3
ba	CHClF-CClF-CF_3
bb	CHF_2-CClF-$CClF_2$
ca	**$CHCl_2$-CF_2-CF_3**
cb	**CHClF-CF_2-$CClF_2$**
cc	CHF_2-CF_2-CCl_2F
da	$CClF_2$-CHCl-CF_3
ea	$CClF_2$-CHF-$CClF_2$
eb	CCl_2F-CHF-CF_3



1.9 – 16.3 years



127 – 1560

GWP Estimated Uncertainty (*this work*)

~50% (<1 year lifetime)
~35% (>2 year lifetime)

Lifetime	~25%
RE	<30% (*depends on lifetime adjustment*)

* Reliable GWP determinations
* Protocol relevant GWPs
* Comparable to uncertainty for "known" compounds

Careful laboratory studies could reduce GWP uncertainty from input parameters to ~20% (>2 year lifetime)

Acknowledgments

NOAA Colleagues

M. Baasandorj
F. Bernard
M. Davis
K. Feierabend
D. Fahey
T. Gierczak
M. Gilles
M. Harwood
C. Howard
E. Jimenez
A. Jubb
S. McKeen
R. Mauldin
M. McGillen
A. Mellouki
J. Orlando
V. Papadimitriou
D. Papanastasiou
R. Portmann
B. Rajakumar
A. Ravishankara
A.-M. Schmoltner
S. Solomon
R. Talukdar
G. Vaghjiani
R. Warren
R. Yokelson

and others !

NASA Data Panel (2015)

Burkholder, Sander, Abbatt, Barker, Huie, Kolb, Kurylo, Orkin, Wilmouth, Wine

and past panel members

Others !!!

CFCs
↓
HCFCs
↓
HFCs
↓

Blank