Modeling Tropospheric Chemistry

Part 1 – processes

Sasha Madronich
National Center for Atmospheric Research
Boulder, Colorado USA
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NCAR

Ideal Gas Law

$PV = Nk_BT$ (equivalent, $PV = NRT$)

$N/V = P/k_BT$ = **2.69×10^{19} molecules cm^{-3}** at STP (273K, 1 atm)

1 ppm = one part / million, 10^{-6} = 2.69×10^{13} molecules cm^{-3} at STP
1 ppb = one part / billion, 10^{-9} = 2.69×10^{10}
1 ppt = one part / trillion, 10^{-12} = 2.69×10^{7}
Can be on atom basis, e.g. carbon ppbC, or molar (volume) basis, ppbv

Scaling to any T, P: $N/V = (273K/T)\ (P/1atm)\ 2.69 \times 10^{19}$ molecules cm^{-3}

1 Dobson Unit = column, compressed to STP, in "milli-centimeters"
= $2.69x^{16}$ molecules cm^{-2}
(used mostly for total O_3, but also for SO_2 and NO_2)

Order of Reaction

First: A → Products k_1, s^{-1}

e.g.: photolysis

radioactive decay

thermal decomposition (but usually more complex, see next slide)

Second: A + B → Products k_2, $cm^3\ molec^{-1}\ s^{-1}$

(2-body, bimolecular)

two important types:

abstraction, e.g. $OH + CH_4 \rightarrow H_2O + CH_3$

addition, e.g. $OH + NO_2 \rightarrow HNO_3$

Third: A + B + C → Products k_3, $cm^6\ molec^{-2}\ s^{-1}$

(3-body, termolecular)

- Very rare at atmospheric pressures: low probability of three-way collision.
- (but the transition state of a bimolecular reaction could live long enough to collide).

$$d[A]/dt = -k_1[A] - k_2[B][A] - k_3[C][B][A] = -d[Products]/dt$$

Uni-Molecular Decomposition: AB → A + B

Thermal decomposition as a multi-step reaction (Lindemann, 1922)

$AB + M \xrightarrow{k_A} AB^* + M$ k_A, activation of excited state AB* by collision with M (AB* = *transition state* or *activated complex*)

$AB^* + M \xrightarrow{k_Q} AB + M$ k_Q, quenching, no decomposition

$AB^* \xrightarrow{k_D} A + B$ k_D, decomposition

$d[AB]/dt = - k_A[M][AB] + k_Q[M][AB^*]$ steady state: $[AB^*]_{ss} = k_A[AB][M]/(k_D + k_Q[M])$

(after some algebra)

$d[AB]/dt = -k_{UNI}[AB]$ where $k_{UNI} = k_A[M]/(1 + k_Q[M]/k_D)$

Low pressure limit: k_A [M] (pressure-dependent)

High pressure limit: $k_A k_D/k_Q$ (not pressure dependent)

Troe (1979) gave a refined expression for k_{uni}

Addition reactions are similar, but in reverse: $A + B \leftrightarrow AB^* \xrightarrow{M} AB$

Photolysis Processes

Photolysis reaction: $AB + h\nu \rightarrow A + B$

Formally first-order:

$$\left.\frac{\mathrm{d[AB]}}{\mathrm{d}t}\right|_{h\nu} = -J[\mathrm{AB}]$$

$$\left.\frac{\mathrm{d[A]}}{\mathrm{d}t}\right|_{h\nu} = \left.\frac{\mathrm{d[B]}}{\mathrm{d}t}\right|_{h\nu} = +J[\mathrm{AB}]$$

Photolysis frequency (s^{-1}) $J = \int_\lambda F(\lambda)\,\sigma(\lambda)\,\phi(\lambda)\,\mathrm{d}\lambda$

(other names: photo-dissociation rate coefficient, J-value)

CALCULATION OF PHOTOLYSIS COEFFICIENTS

$$J\ (s^{-1}) \quad = \quad \int_{\lambda} F(\lambda)\ \sigma(\lambda)\ \phi(\lambda)\ d\lambda$$

$F(\lambda)$ = spectral actinic flux, quanta cm^{-2} s^{-1} nm^{-1}

$\propto$ probability of photon near molecule.

$\sigma(\lambda)$ = absorption cross section, cm^2 $molec^{-1}$

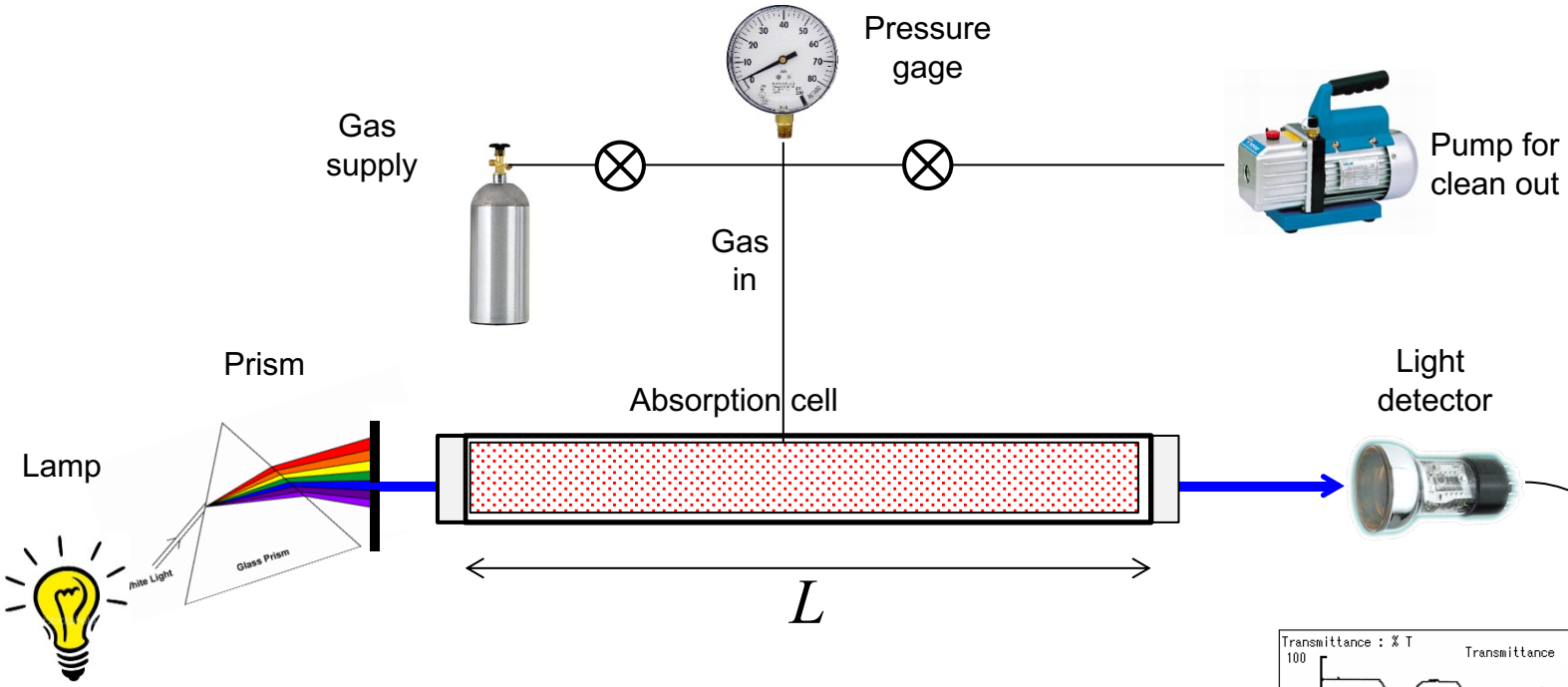
$\propto$ probability that photon is absorbed.

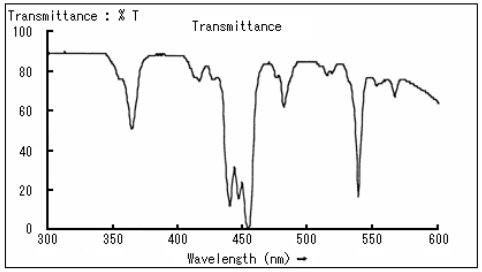
$\phi(\lambda)$ = photodissociation quantum yield, molec $quanta^{-1}$

$\propto$ probability that absorbed photon causes dissociation.

detail lecture by S. Madronich, Wed. 11:30…

Measurement of Absorption Cross Section σ(λ)



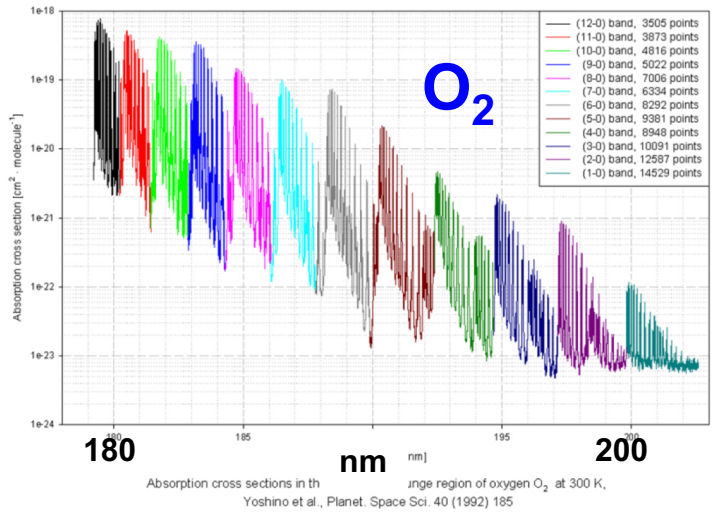


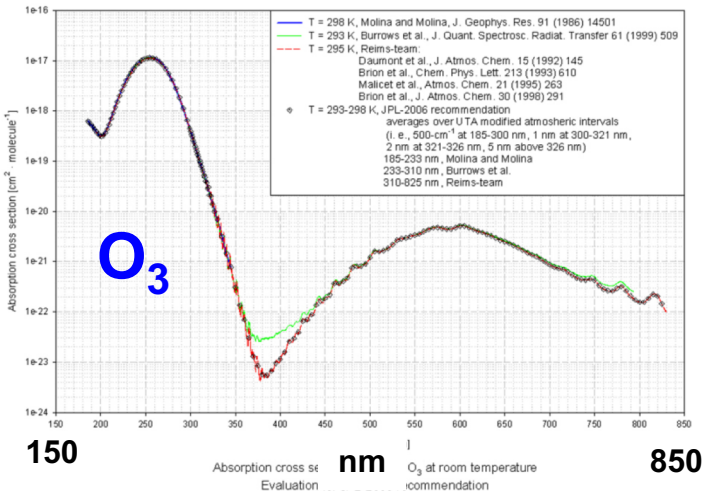
Transmittance = I / I_o = exp(-σ n L)

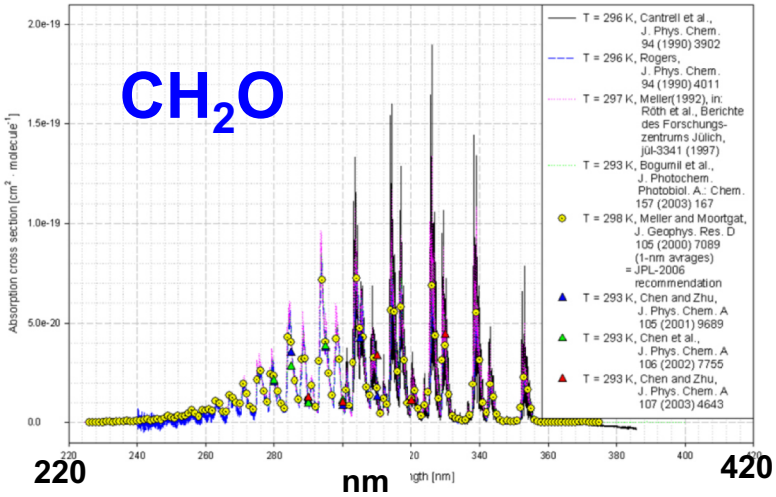
σ = -1/(nL) ln(I / I_o)

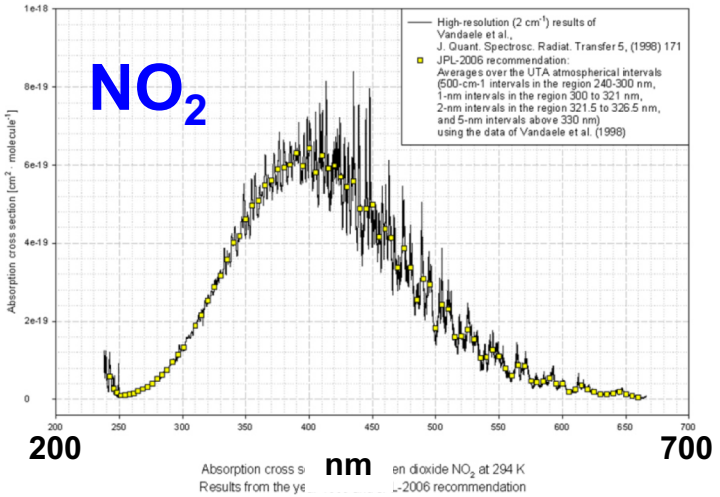
Easy: measure pressure ($n = P/RT$), and relative change in light: I / I_o

Absorption cross sections $\sigma(\lambda, T)$









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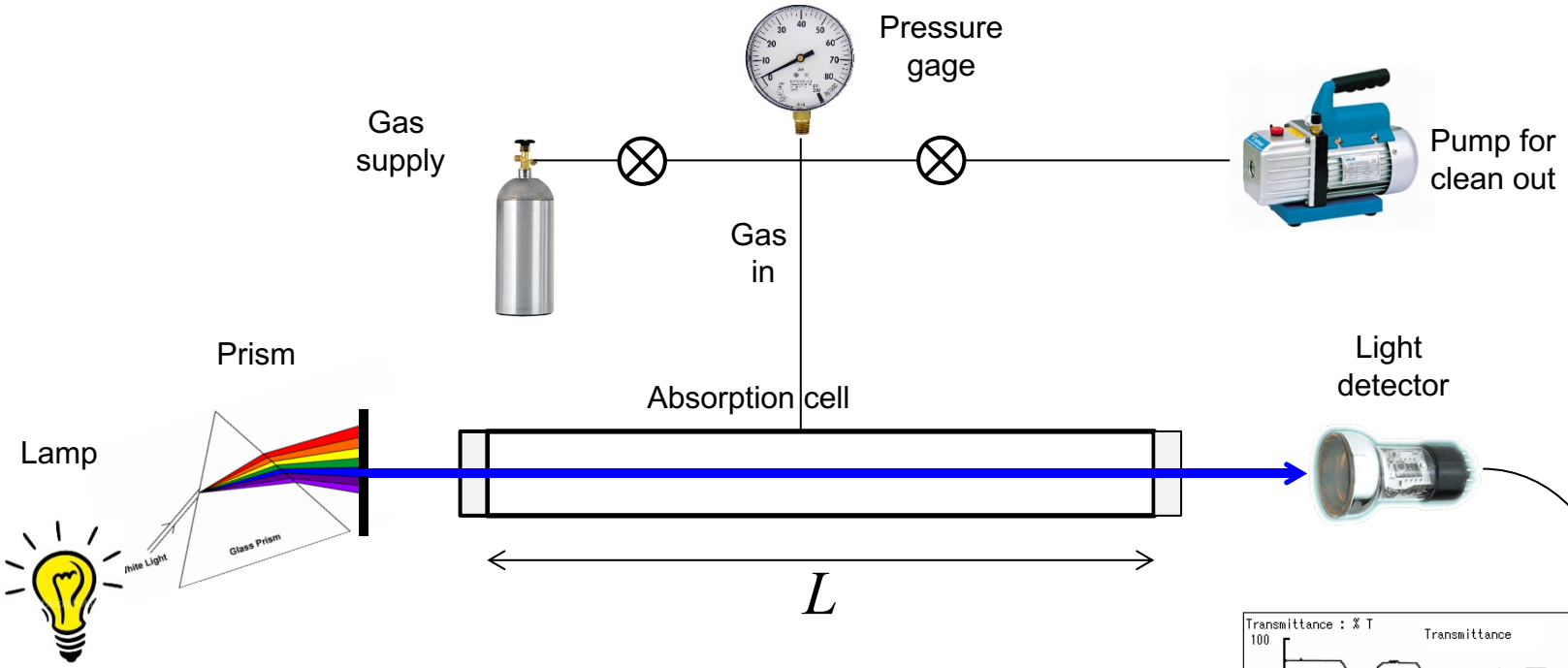
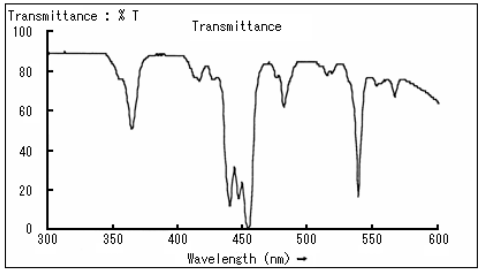
Measurement of Quantum Yields $\phi(\lambda)$





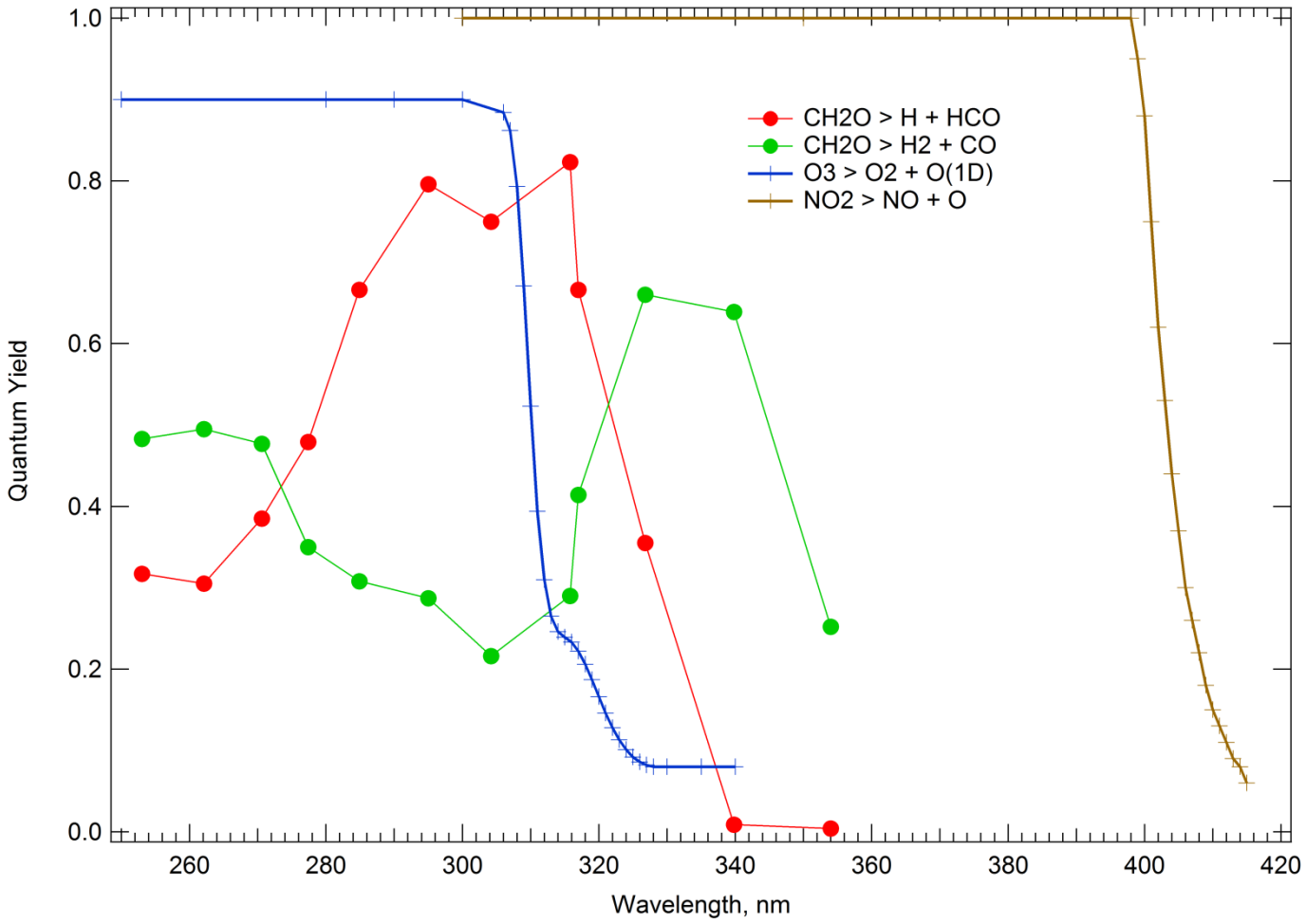
Transmittance = I / I_o = exp(-σ n L)

Quantum Yield = number of breaks per photon absorbed

$\phi = \Delta n / \Delta I$

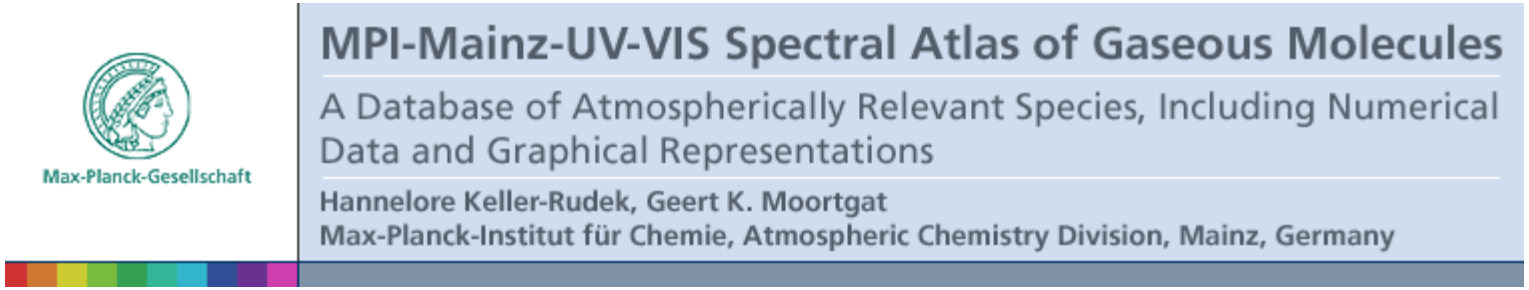
Difficult: must measure absolute change in n (products) and I (photons absorbed)

Photo-dissociation Quantum Yields $\phi(\lambda,T, P)$

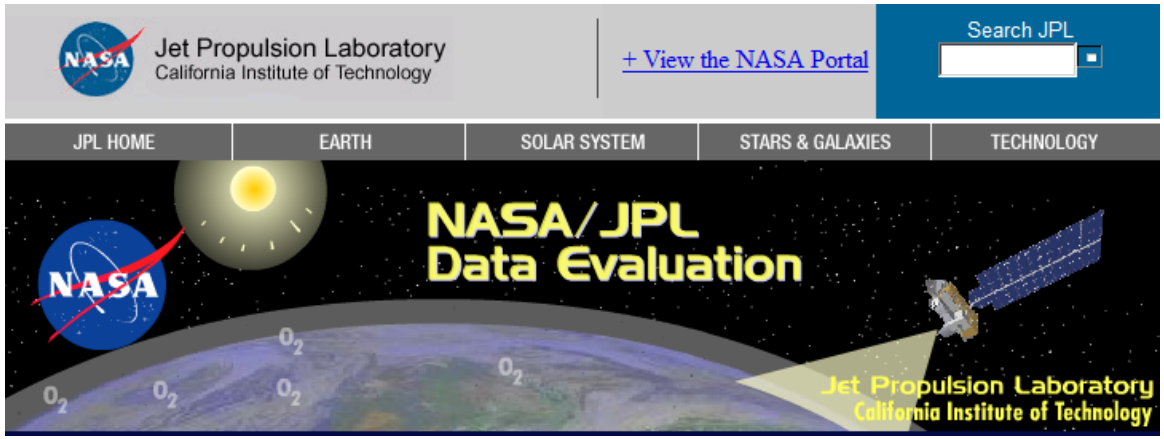


Compilations of Cross Sections & Quantum Yields

http://www.atmosphere.mpg.de/enid/2295



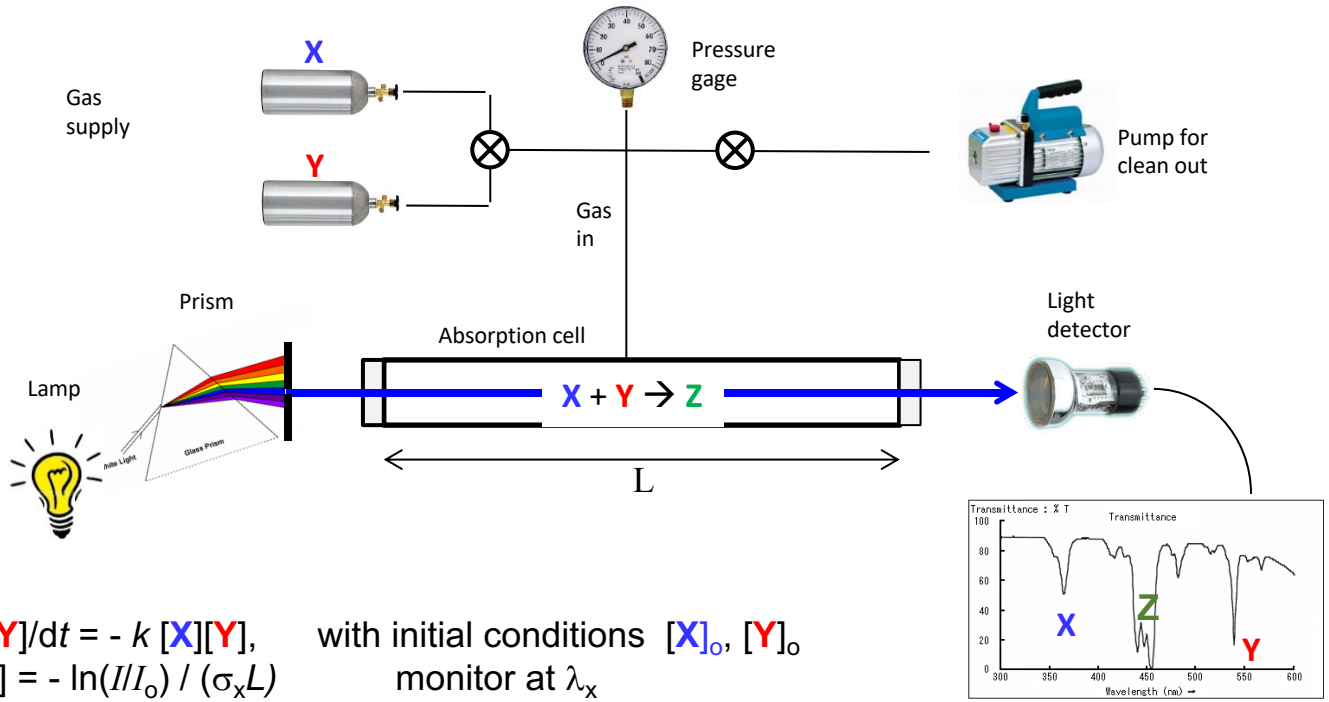
http://jpldataeval.jpl.nasa.gov/



Some Important Photolysis Reactions

$O_2 + h\nu\ (\lambda < 240\ nm) \rightarrow O + O$	source of O_3 in stratosphere
(detailed lectures by Susan Solomon and Doug Kinnison, later today)	
$O_3 + h\nu\ (\lambda < 340\ nm) \rightarrow O_2 + O(^1D)$	source of OH in troposphere
$NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow NO + O(^3P)$	source of O_3 in troposphere
$CH_2O + h\nu\ (\lambda < 330\ nm) \rightarrow H + HCO$	source of HOx, everywhere
$H_2O_2 + h\nu\ (\lambda < 360\ nm) \rightarrow OH + OH$	source of OH in remote atm.
$HONO + h\nu\ (\lambda < 400\ nm) \rightarrow OH + NO$	source of radicals in urban atm.

Measurement of Bimolecular Rate Constants: X + Y → Z



d[X]/dt = d[Y]/dt = - k [X][Y], with initial conditions $[X]_o$, $[Y]_o$

Measure [X] = - ln(I/I_o) / ($\sigma_x L$) monitor at λ_x

[Y] = - ln(I/I_o) / ($\sigma_y L$) monitor at λ_y

So can estimate k *e.g.*, k = -dln[X]/dt /[Y]

Repeat at different temperatures: simple Arrhenius $k(T) = A\, e^{-Ea/RT}$

if T ↑ : k ↑ *if Ea > 0 (e.g. abstraction)*

k ↓ *if Ea < 0 (e.g. addition)*

If lucky to see also product $[Z]_t$, can get products/branching

Chemical Rate Equations

A + B → C + D k_1

C → B + F k_2

….

$d[A]/dt = - k_1 [A][B]$

$d[B]/dt = - k_1 [A][B] + k_2[C]$

$d[C]/dt = +k_1 [A][B] – k_2[C]$

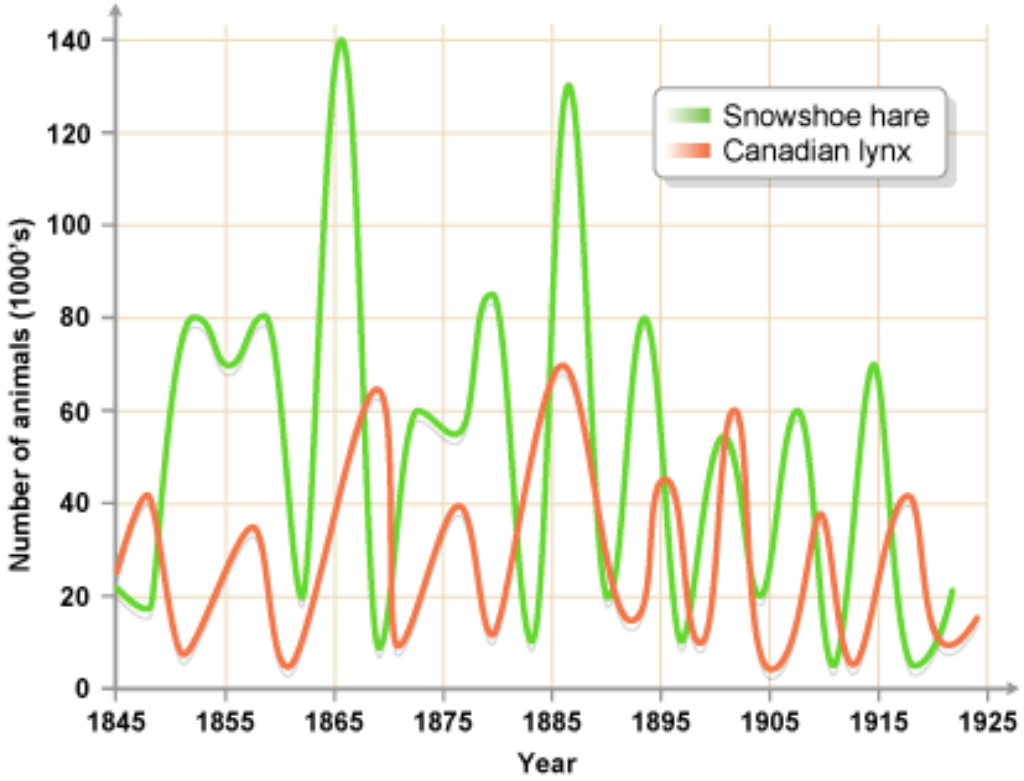
In general: $\mathbf{y}(t) =$ concentration vector

$\mathbf{S}(t, \mathbf{y}) =$ chemical source/sink function

$$\frac{\partial}{\partial t}\mathbf{y} = \mathbf{S}(t, \mathbf{y}), \qquad \mathbf{y}(t_o) = \mathbf{y_o}$$

$$S_i = a_i + \sum_i b_{i,j}\, y_j + \sum_{j,k} c_{i,jk} y_j y_k$$

Chemistry Rates : Generalized Lotka-Volterra Equations



Prey-predator population dynamics:

Rabbits multiply by grazing, eaten by foxes

Foxes multiply when rabbits abundant,

but then eat too much

Numerical Solution of Chemical Rate Equations

Time stepping: $\mathbf{y_n}(t_n) \rightarrow \mathbf{y_{n+1}}(t_{n+1})$

- Explicit (forward) Euler forward Scheme

$$\boldsymbol{y_{n+1}} = \boldsymbol{y_n} + \Delta t\, \mathbf{S}(t_n, \boldsymbol{y_n}), \qquad \Delta t = t_{n+1} - t_n$$

Only stable if $\Delta t \leq \frac{2}{max_j|\mathrm{Re}(\lambda_j)|}$ where λ_j are the eigenvalues of the Jacobian matrix $\mathbf{J} = \frac{\partial \mathbf{S}}{\partial \mathbf{y}}$

- Implicit (backward) Euler scheme

$$\mathbf{y_{n+1}} = \mathbf{y_n} + \Delta t\, \mathbf{S}(t_{n+1}, \mathbf{y_{n+1}})$$

Unconditionally stable (but stability does not imply accuracy).
Solution not straightforward if **S** is non-linear, often iterative.
For linear systems, becomes exact as $t \rightarrow \infty$

Detailed Lecture by Andrew Conley, later today…

Concerted Tropospheric Chemical Reactions
Major Environmental Issues

- Tropospheric ozone
  - Auto-catalytic formation, role of NOx
- Tropospheric OH radicals
  - Global self-cleaning capacity, tropospheric lifetimes
- Secondary Organic Aerosols
  - Organic complexity (hydrocarbon oxidation)
  - Many other important issues, e.g.
    - Sulfur (SO_2, H_2SO_4, DMS), NH_3, halogens, Hg, POPs,…
    - Chemistry in condensed phases and interfaces

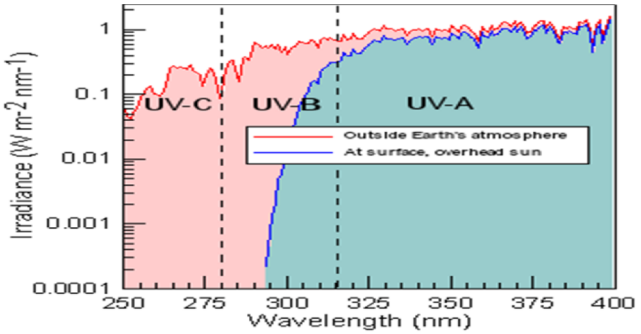
Tropospheric Ozone Formation

- Laboratory studies show that O_3 is made almost exclusively by the reaction:

$$O_2 + O + M \rightarrow O_3 + M$$

- But no tropospheric UV-C radiation to break O_2

$$O_2 + h\nu \ (\lambda < 242\ nm) \rightarrow O + O$$



- *Haagen-Smit(1950s)* - Los Angeles smog:

Urban ozone (O_3) is generated when air containing hydrocarbons and nitrogen oxides (NOx = NO + NO_2) is exposed to tropospheric UV radiation

The Nitrogen Family

N	nitrogen atoms – negligible at room temperature T
N_2	molecular nitrogen

Nitrogen oxides : $NOx \equiv NO + NO_2$

NO	nitric oxide is 90-95% of direct emissions
NO_2	nitrogen dioxide is 5-10% of direct emissions, but more is made from NO + oxidants in the atmosphere

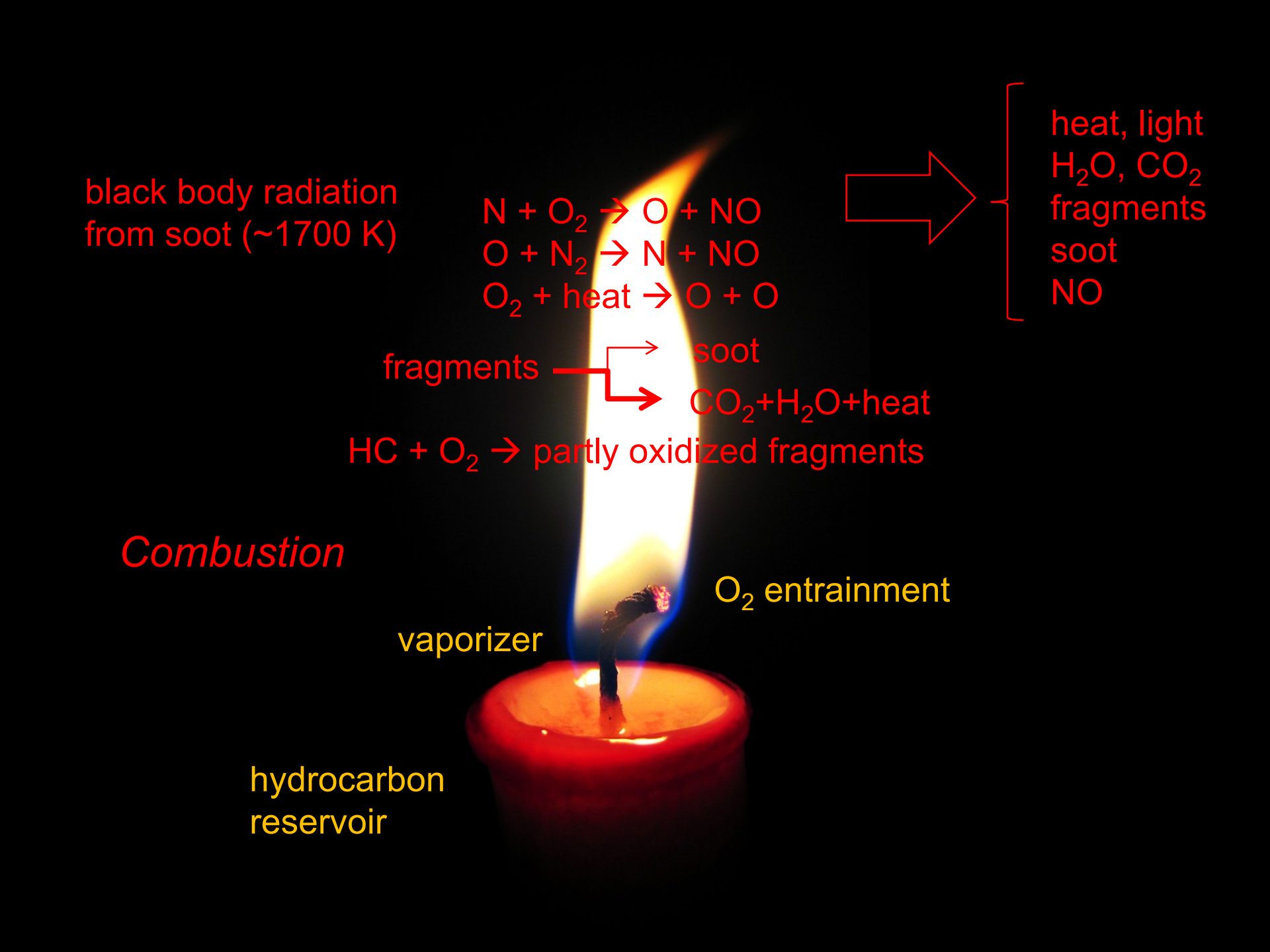
Zeldovich mechanism at high T (flames, engines, lightning):

O_2 + heat → O + O

O + N_2 → N + NO

N + O_2 → O + NO

(NO is the cross-product of scrambling N_2 and O_2 at high T)


black body radiation from soot (~1700 K)
N + O2 → O + NO
O + N2 → N + NO
O2 + heat → O + O
heat, light
H2O, CO2
fragments
soot
NO
fragments
soot
CO2+H2O+heat
HC + O2 → partly oxidized fragments
Combustion
O2 entrainment
vaporizer
hydrocarbon reservoir

(some other nitrogen species)

NO_3	nitrate radical
N_2O_5	dinitrogen tetroxide
HONO	nitrous acid
$HONO_2$	nitric acid
CH_3ONO_2	methyl nitrate
N_2O	nitrous oxide (laughing gas)
NH_3	ammonia
NH_2CH_3	methyl amine

Tropospheric O_3 Formation (some)

NO_2 photo-dissociation is the source of O atoms that make tropospheric O_3

$$NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

Net: $NO_2 + h\nu + O_2 \rightarrow NO + O_3$

$j_{NO2} \sim 10^{-2}\ s^{-1}$ at high sun

Tropospheric O_3 Formation – but not enough!

- NO_2 photo-dissociation makes some O_3, but not enough. Two problems:

Usually O_3 ~ 20 - 500 ppb >> NO_2 ~ 1 – 10 ppb

Reversal by the reaction:

$$NO + O_3 \rightarrow NO_2 + O_2$$

Tropospheric O_3 Formation – the role of VOCs

- Initiation by UV radiation (*Levy, 1970*):

  $O_3 + h\nu\ (\lambda < 330\ nm) \rightarrow O^*(^1D) + O_2$

  $O^*(^1D) + H_2O \rightarrow \cdot OH + \cdot OH$

  Net: $O_3 + h\nu + H_2O \rightarrow OH + OH$

- Hydrocarbon consumption (oxygen entry point):

  $\cdot OH + RH \rightarrow R\cdot + H_2O$

  $R\cdot + O_2 + M \rightarrow ROO\cdot + M$

- Single-bonded oxygen transferred to NOx:

  $ROO\cdot + NO \rightarrow RO\cdot + NO_2$

- NOx gives up oxygen atoms (as before):

  $NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow NO + O$

  $O + O_2 + M \rightarrow O_3 + M$

Tropospheric O_3 Formation - more

- Propagation

$RO\cdot + O_2 \rightarrow R'CO + HOO\cdot$

$HOO\cdot + NO \rightarrow \cdot OH + NO_2$

every NO → NO_2 conversion makes O_3

except $NO + O_3 \rightarrow NO_2 + O_2$

- Termination

$\cdot OH + NO_2 + M \rightarrow HNO_3 + M$

$HOO\cdot + HOO\cdot + M \rightarrow H_2O_2 + M$

$HOO\cdot + O_3 \rightarrow \cdot OH + 2\ O_2$

The 10-Reaction Mechanism

$Ox \equiv NO_2 + O_3$

$HOx \equiv \cdot OH + HOO + RO + ROO$

$NOx \equiv NO + NO_2$

	ΔOx	ΔHOx	ΔNOx
Initiation by photo-oxidation			
$O_3 + h\nu + H_2O \rightarrow 2\ \cdot OH + O_2$	-1	+2	na
$\cdot OH + RH + O_2 + M \rightarrow ROO\cdot + H_2O + M$	0	0	na
Partitioning by NOx			
$ROO\cdot + NO \rightarrow RO\cdot + NO_2$	+1	0	0
$NO_2 + h\nu + O_2 \rightarrow O_3 + NO$	0	na	0
$NO + O_3 \rightarrow NO_2 + O_2$	0	na	0
Propagation			
$RO\cdot + O_2 \rightarrow HOO\cdot + R'CO$	0	0	na
$HOO\cdot + NO \rightarrow \cdot OH + NO_2$	+1	0	0
Termination			
$\cdot OH + NO_2 + M \rightarrow HNO_3 + M$	-1	-1	-1
$HOO\cdot + HOO\cdot + M \rightarrow H_2O_2 + O_2 + M$	0	-2	na
$HOO\cdot + O_3 \rightarrow \cdot OH + 2\ O_2$	-1	-1	na

Global Photo-oxidation (self-cleaning) Capacity

Solar UV radiation

Oxidation, e.g.:

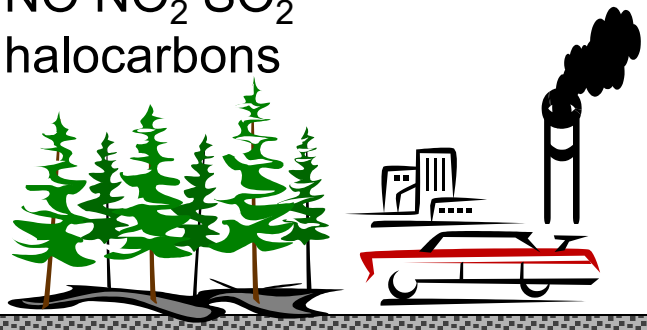
$CH_4 + OH \rightarrow \ldots \rightarrow CO_2 + H_2O$

Insoluble → Soluble

Emissions

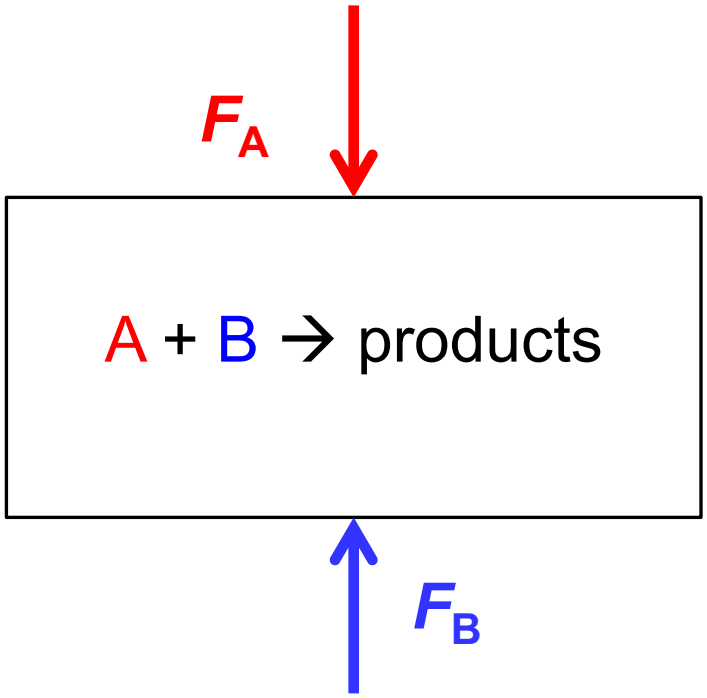
Deposition (dry, wet)

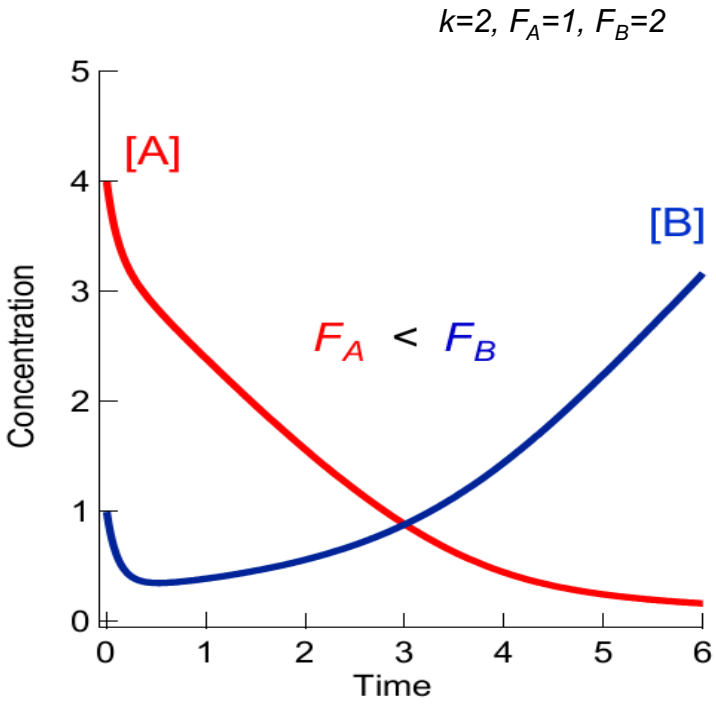
CO CH_4 C_mH_n
NO NO_2 SO_2
halocarbons

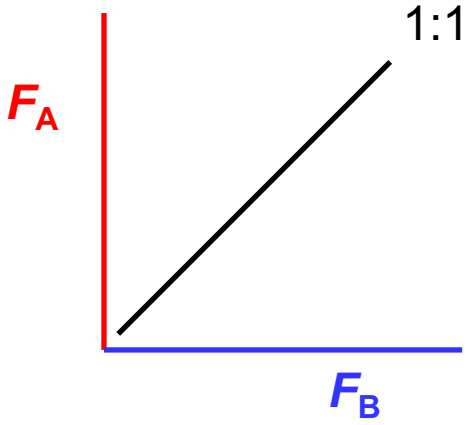


H_2SO_4, HNO_3, HCl, Cl^-,CH_2O

Bimolecular Instability







Simple system is stable only along 1:1 line

Tropospheric Self-cleaning Need

Global emissions of reduced compounds, Teramoles/year

	Natural	Anthropogenic	Total
CO	54	54	108
CH_4	12	28	40
VOCs	60	20	80
NO	1	3	4
Total	128	105	233

Annual production of OH must be > sum of these emissions

OH Sinks vs. Sources (Teramoles/year)

OH sources: O_3 photolysis

O_3 from strat. ~ 10

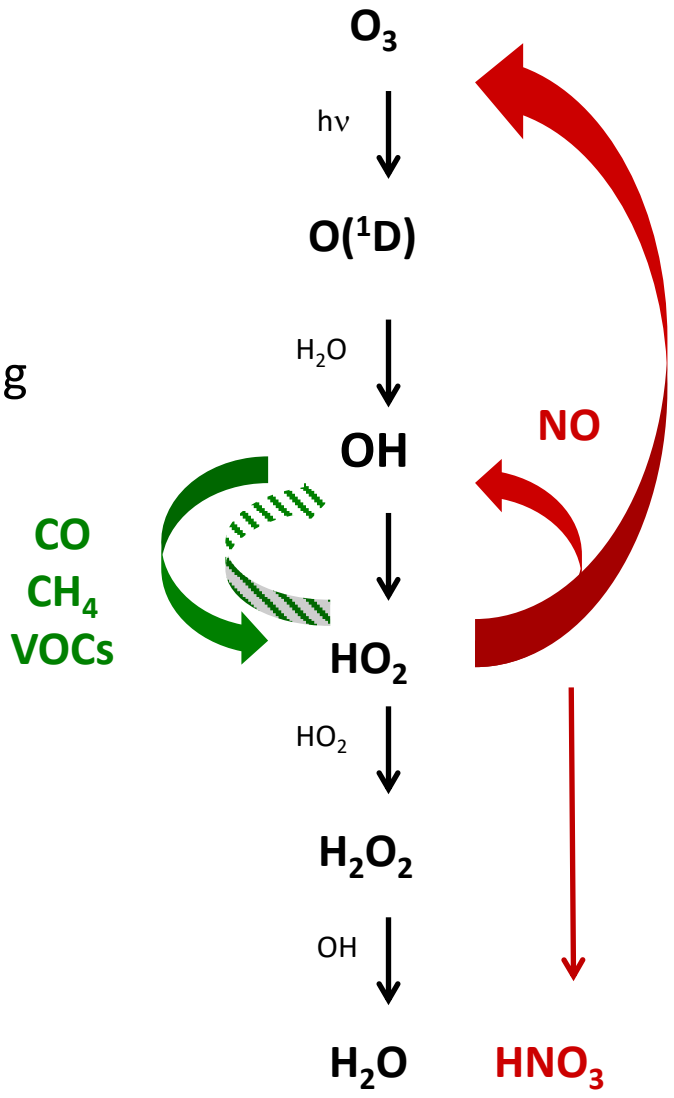
Tropospheric Ox-HOx-NOx cycling

OH sinks:	pre-ind.	current
CO	54	108
CH_4	12	40
Other VOCs	60	80
TOTAL	128	228

NOx Sources:

NO	1	4

OH recycling from biogenic VOC chemistry?



Is OH "Buffered"?

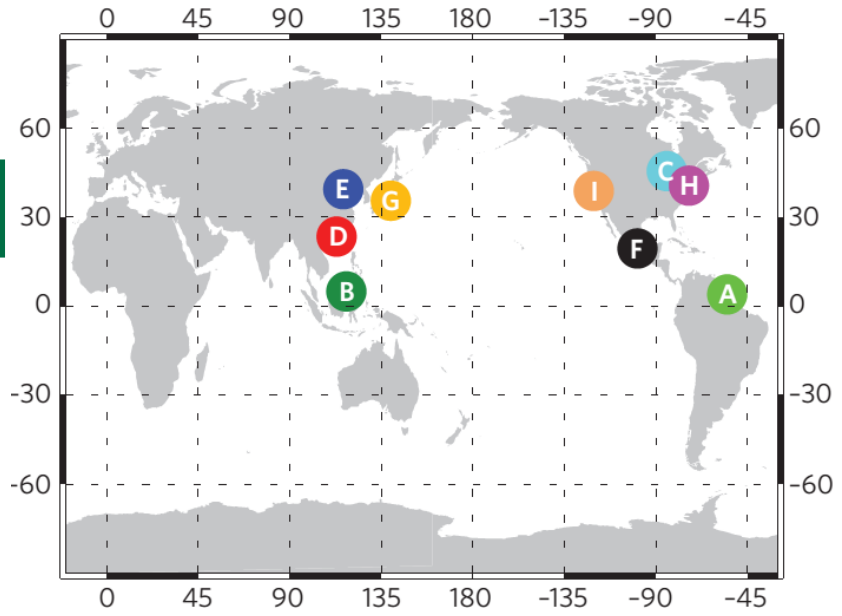
nature geoscience

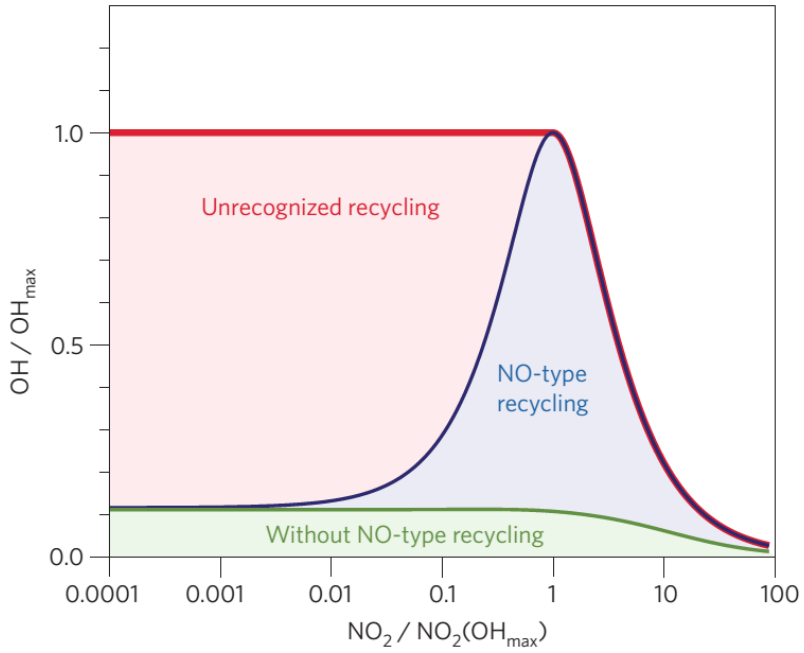
PROGRESS ARTICLE

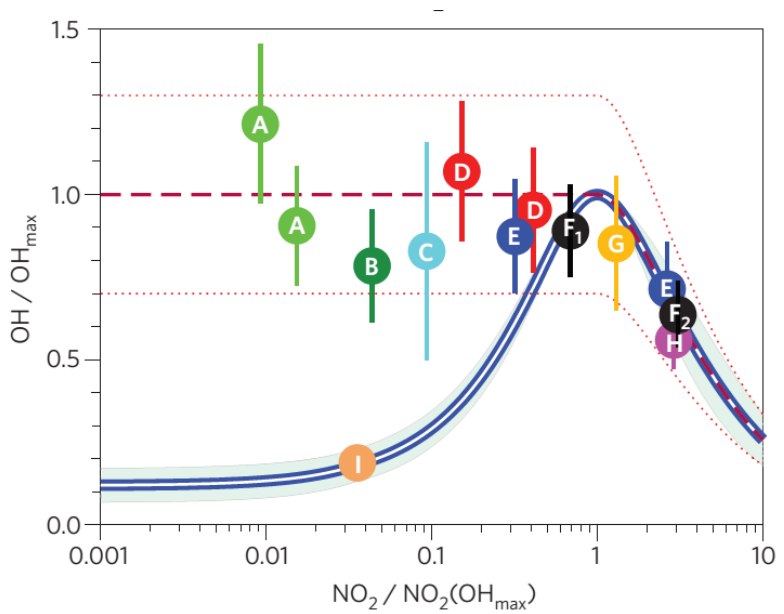
PUBLISHED ONLINE: 13 JULY 2014 | DOI: 10.1038/NGEO2199

Maximum efficiency in the hydroxyl-radical-based self-cleansing of the troposphere

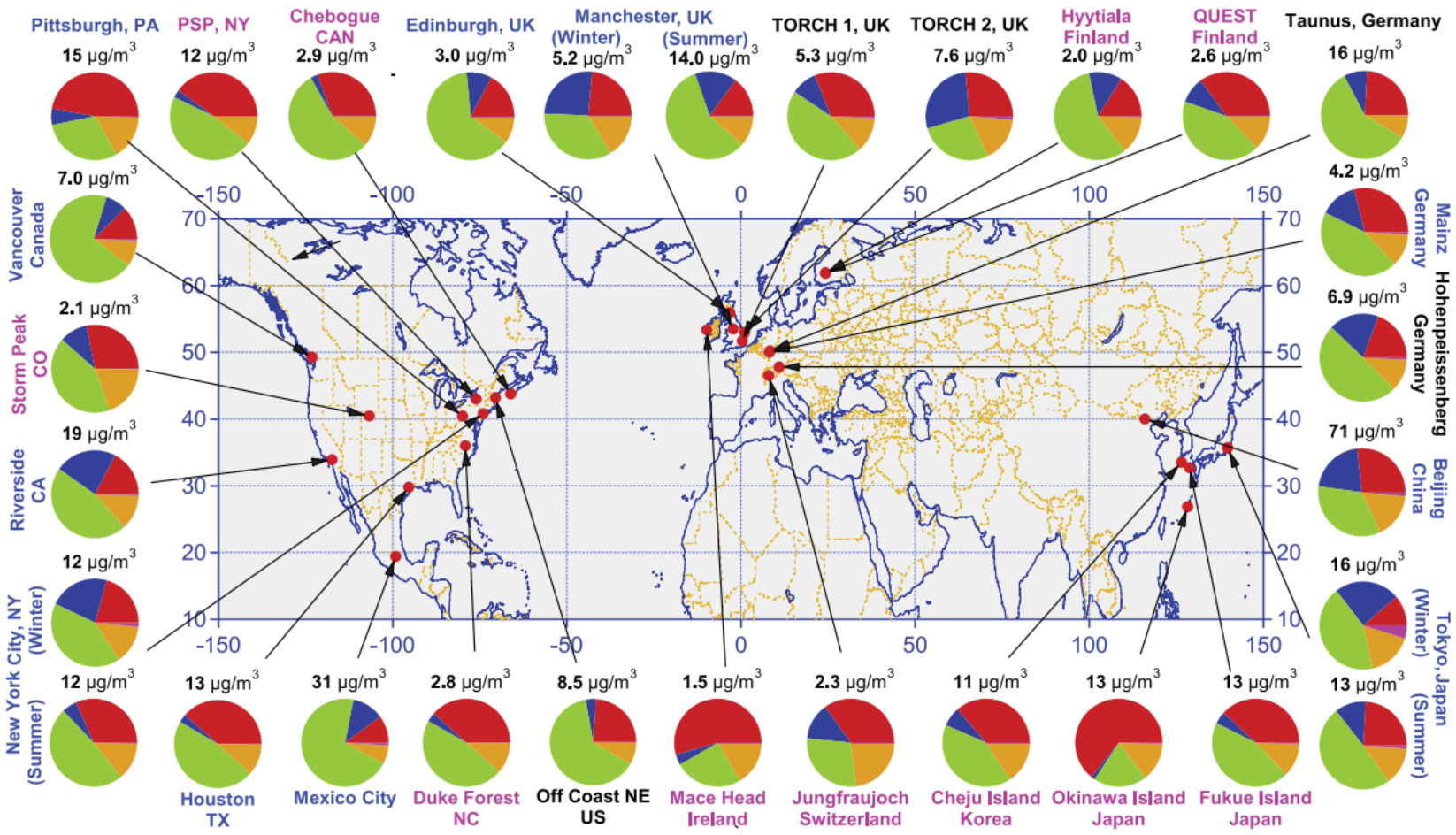
Franz Rohrer[1*†], Keding Lu[1,2†], Andreas Hofzumahaus[1], Birger Bohn[1], Theo Brauers[1‡], Chih-Chung Chang[3], Hendrik Fuchs[1], Rolf Häseler[1], Frank Holland[1], Min Hu[2], Kazuyuki Kita[4], Yutaka Kondo[5], Xin Li[1,2], Shengrong Lou[6], Andreas Oebel[1], Min Shao[2], Limin Zeng[2], Tong Zhu[2], Yuanhang Zhang[2*] and Andreas Wahner[1]







UBIQUITY OF ORGANIC AEROSOLS



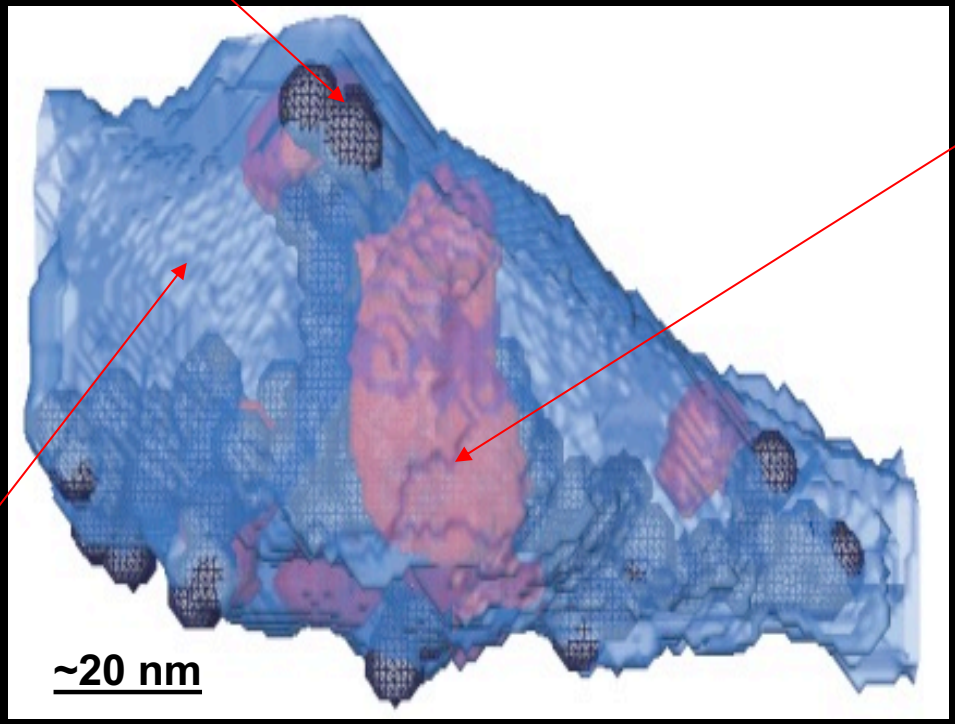
ORGANIC SULFATE NITRATE AMMONIUM CHLORIDE

Qi Zhang et al., GRL 2007

Individual particles have complex morphology and composition

Soot (black spherules)

Sulfate (red)



Organic material (blue)

Adachi, Chung, and Buseck, 2009

Biogenic VOC Emissions, ~1000 Tg / year

Table 6. Global annual total emissions simulated for the year 2000 using MEGAN2.1 algorithms in CLM4.

Compound Class	Compounds	Emissions ($Tg\,yr^{-1}$)
Isoprene	Isoprene	535
α-Pinene	α-Pinene	66.1
t-β-Ocimene	t-β-Ocimene	19.4
β-Pinene	β-Pinene	18.9
Limonene	Limonene	11.4
Sabinene	Sabinene	9.0
Myrcene	Myrcene	8.7
3-Carene	3-Carene	7.1
Other Monoterpenes	Camphene	4.0
	β-phellandrene	1.5
	Terpinolene	1.3
	Additional 31 monoterpenes	14.9
α-Farnesene	α-Farnesene	7.1
β-Caryophyllene	β-Caryophyllene	7.4
Other Sesquiterpenes	β-Farnescene	4.0
	α-Humulene	2.1
	α-Bergamotene	1.3
	Additional 27 sesquiterpenes	7.1
232-MBO	232-MBO	2.2
Methanol	Methanol	99.6
Acetone	Acetone	43.7
Bidirectional VOC	Ethanol	20.7
	Acetaldehyde	20.7
	Formaldehyde	5.0
	Acetic acid	3.7
	Formic acid	3.7
Stress VOC	Ethene	26.9
	cis-3-hexenal	4.9
	DMNT	4.9
	cis-3-hexenol	2.9
	Additional 11 stress VOC	7.8
Other VOC	Propene	15.8
	Butene	8.0
	Homosalate	2.0
	Geranyl acetone	0.8
	Additional 45 other VOC	5.5
Total VOC	Sum of 146 VOC	1007
CO	CO	81.6
Total	VOC and CO	1089

Guenther et al., GMD 2012

Anthropogenic Hydrocarbons Emissions ~ 150 Tg/yr

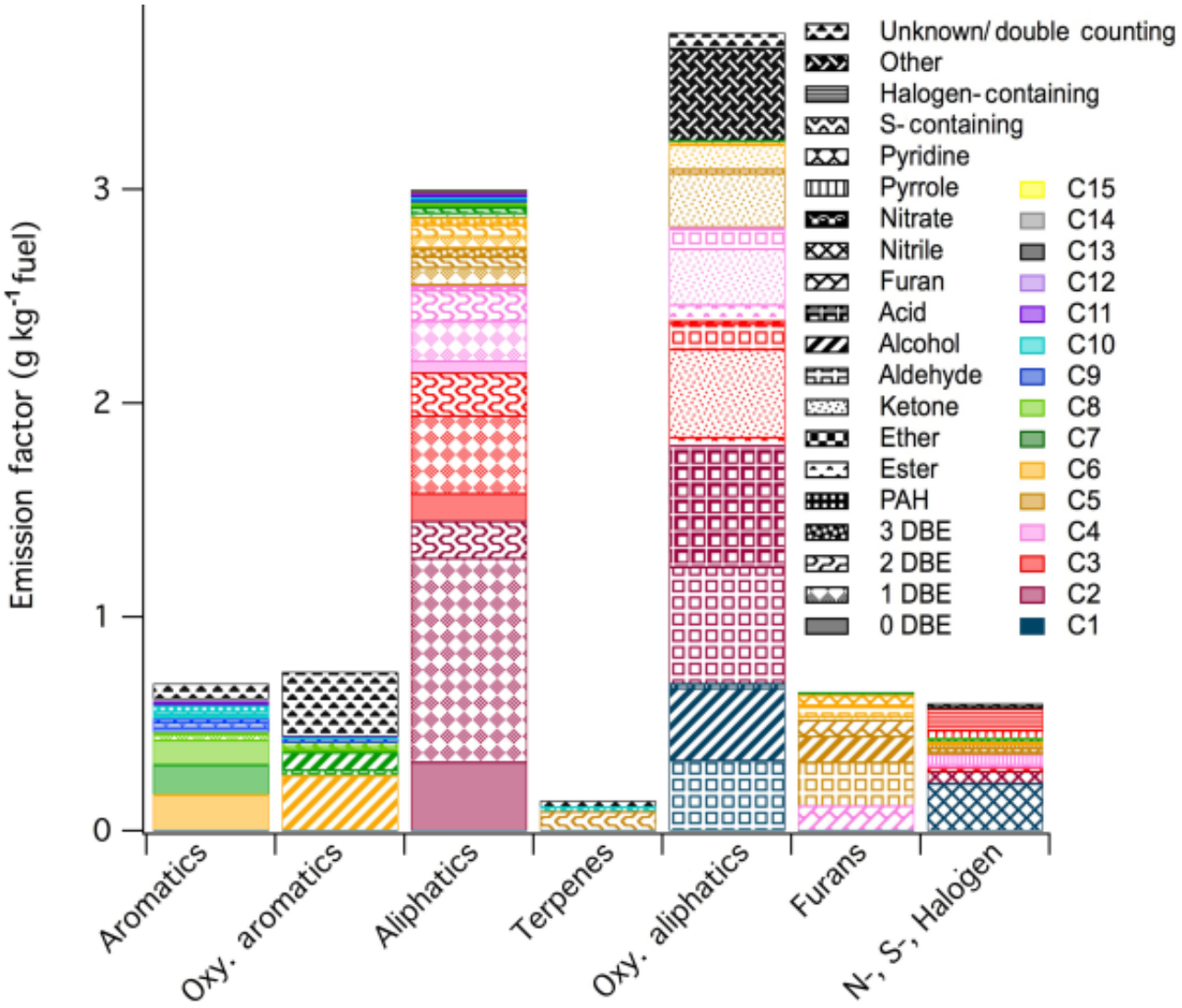
Concentrations in Mexico City PBL, C-130 aircraft 2006 March averages

	24 h[b]	daytime[c]
Ethane	5101	6447
Propane	30 809	37 536
n-Butane	12 569	20 332
i-Butane	4221	8266
2,2-Dimethylbutane	469	656
i-Pentane	4555	8380
n-Pentane	3012	5016
n-Hexane	1628	4493
2,3-Dimethylbutane	2550	2959
2-Methylpentane	1919	2894
3-Methylpentane	1324	2057
2,2,4-Trimethylpentane	718	1045
n-Heptane	367	679
Cyclopentane	251	365
2,3,4-Trimethylpentane	286	335
2,4-Dimethylpentane	198	301
Cyclohexane	235	301
n-Octane	154	245
Decane	154	224
n-Nonane	102	123

	24 h[b]	daytime[c]
Ethene	6908	7808
Propene	1756	1765
1-Butene + *i*-Butene	880	1022
1-Pentene	101	264
3-Methyl-1-butene	58	126
1,3-Butadiene	152	122
2-Methyl-2-butene	219	606
Trans+cis-2-Butene[e]	249	770
Trans+cis-2-Pentene[e]	243	546
Toluene	8944	10 649
Benzene	931	1703
Ethylbenzene	532	938
m-Xylene	452	845
1,2,4-Trimethylbenzene	434	834
o-Xylene	238	404
p-Xylene	180	373
3-Ethyltoluene	118	244
4-Ethyltoluene	68	138
1,3,5-Trimethylbenzene	70	115
2-Ethyltoluene	52	108

Apel et al., ACP, 2010

Pyrogenic VOC Emissions 40-100 Tg/yr



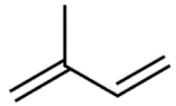
Missoula Fire Lab 500+ VOCs identified

Rice straw

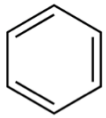
Hatch et al. ACP 2017

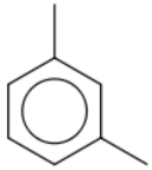
Hydrocarbons (double C=C bonds)

- **Alkenes**
  - ethene (ethylene) $CH_2=CH_2$
  - propene (propylene) $CH_2=CHCH_3$
  - …
  - 2-methyl 1,3 butadiene (isoprene) $CH_2=C(CH_3)CH=CH_3$

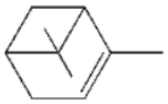


- **Aromatics**
  - benzene C_6H_6
  - toluene $C_6H_5CH_3$
  - xylenes (o,p,m) $C_6H_5(CH_3)_2$
  - …

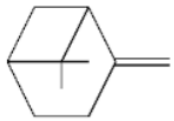




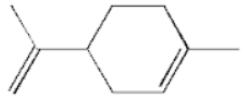
- **Terpenes**
  - $C_{10}H_{16}$



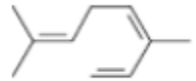
α-pinene



β-pinene



limonene



β-ocimene

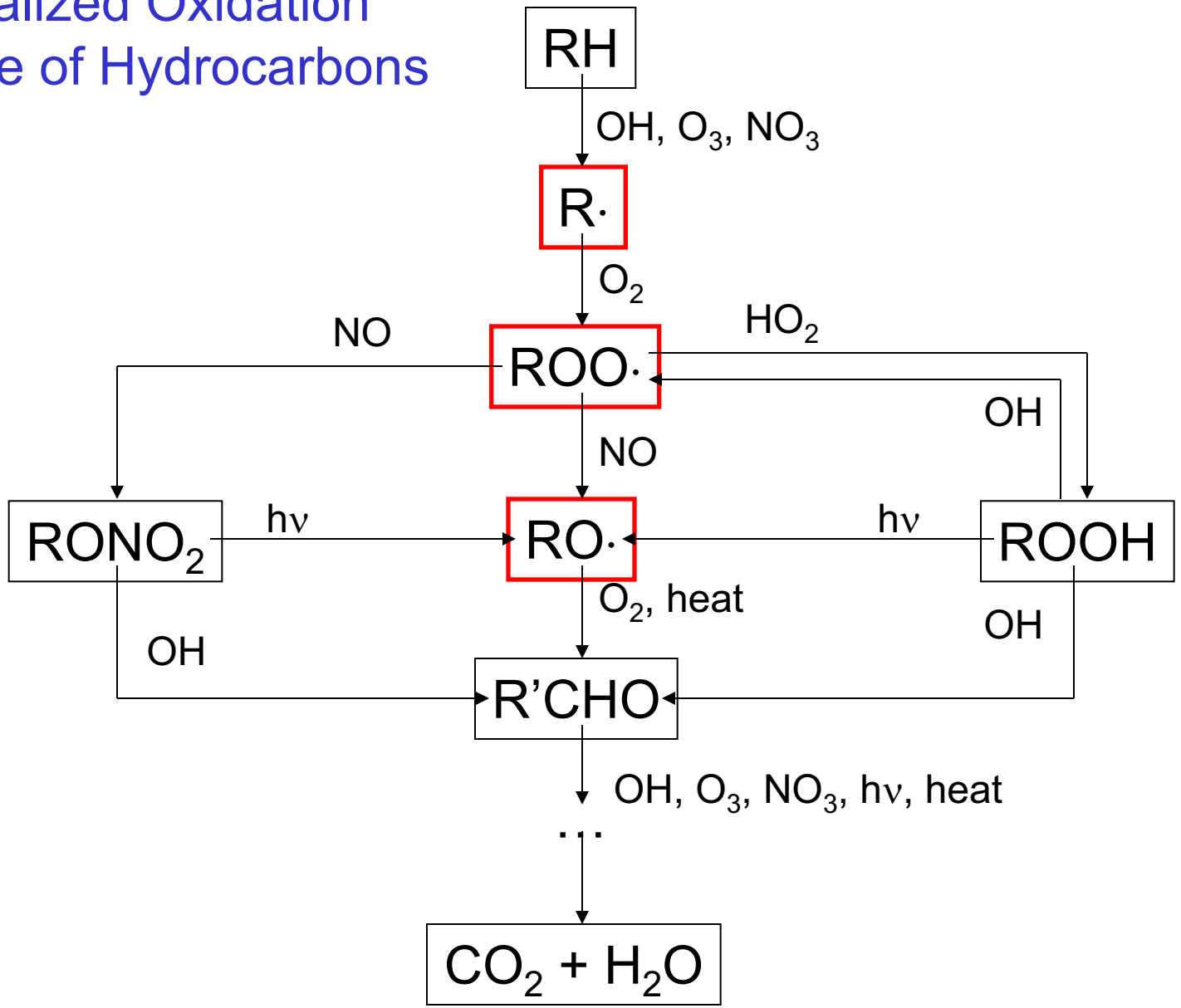
Functional Groups in Substituted Hydrocarbons

- Alcohols, -OH
  - methanol, CH_3OH
  - ethanol, CH_3CH_2OH
- Aldehydes, -CHO
  - formaldehyde, HCHO
  - acetaldehyde, CH_3CHO
- Ketones, -CO-
  - acetone, CH_3COCH_3
  - MEK, $CH_3COCH_2CH_3$
- Carboxylic acids, -CO(OH)
  - formic, HCO(OH)
  - acetic, $CH_3CO(OOH)$
- Organic hydroperoxides, -OOH
  - methyl hydroperoxide, $CH_3(OOH)$
- Organic peroxy acids, -CO(OOH)
  - peracetic, $CH_3CO(OOH)$
- Organic nitrates, $-ONO_2$
  - methyl nitrate, $CH_3(ONO_2)$
  - Ethyl nitrate, $CH_3CH_2(ONO_2)$
- Peroxy nitrates, $-OONO_2$
  - methyl peroxy nitrate, $CH_3(OONO_2)$
- Acyl peroxy nitrates, $-CO(OONO_2)$
  - PAN, $CH_3CO(OONO_2)$

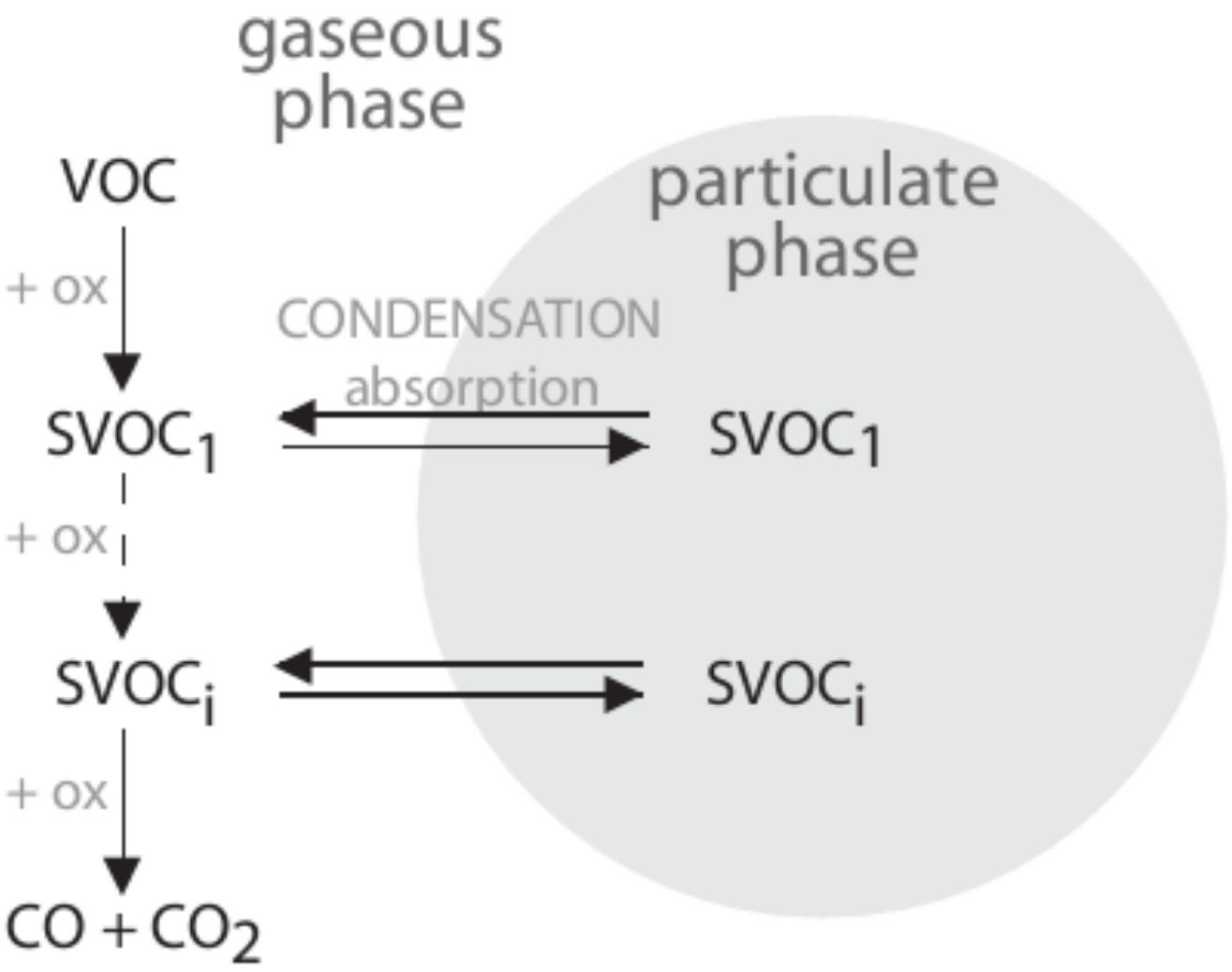
Atmospheric Organic Radicals

- Alkyl (carbon-centered)
  - $\cdot CH_3$ methyl
  - $\cdot CH_2CH_3$ ethyl
  - $\cdot CH_2CH_2CH_3$ propyl
- Peroxy, -OO·
  - $CH_3OO\cdot$ methyl peroxy
  - $CH_3CH_2OO\cdot$ ethyl peroxy
- Alkoxy, -O·
  - $CH_3O\cdot$ methoxy
  - $CH_3CH_2O\cdot$ ethoxy
- Acyl, CO(OO·)
  - $CH_3CO(OO\cdot)$ acetyl
- Criegee, ·C(OO·)
  - $\cdot CH_2OO\cdot$ from $O_3 + C_2H_4$
  - $CH_3\cdot CHOO\cdot$ from $O_3 + C_3H_6$

Generalized Oxidation Sequence of Hydrocarbons



Brasseur, Tyndall, Orlando, 1999



Detailed lectures on aerosols by Jerome Fast, Mary Barth tomorrow…

Tropospheric Gas-Phase Chemical Mechanisms

- Heuristic:

  ~10 reactions, 5 species [*Seinfeld and Pandis, 1997*]

- Typical 3D model used for air quality:

  100 - 300 reactions, 100 species

  CB-IV, CB-V [*Gery,* 1989]

  RADM, RACM [*Stockwell*, 1990; 1997]

  SAPRC99 [*Carter*, 2000]

  MOZART [*Emmons et al*., 2010]

- Typical 0D (box) models used for sensitivity studies:

  3,000 - 10,000 reactions, 1000 species

  NCAR Master Mechanism [*Madronich and Calvert, 1990*]

  Leeds Master Chemical Mechanism [*Jenkin et al., 1997*]

- Hyper-explicit (computer-aided) mechanisms:

  10^6 - 10^7 reactions, 10^5 – 10^6 species

  GECKO-A [*Aumont et al. 2005; Lee-Taylor et al. 2011*]

End part 1