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JÜLICH
FORSCHUNGSZENTRUM

1st QUALI-START-UP SCIENCE LECTURES
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Photochemistry and Radical Chemistry

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Troposphere (IEK-8)

Outline

- Self-cleaning of the atmosphere
- Chemistry of OH, HO_2, and RO_2 radicals in the troposphere and the formation of secondary pollutants
- Measurement and observation of atmospheric radicals
- Summary

Emission of Air Pollutants

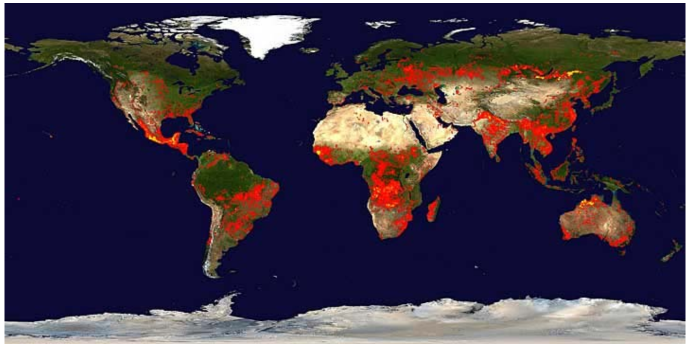
What happens to emitted gases in the atmosphere?

transportation

biomass burning

energy production
and industry

volcanoes



global fire activities

farming

Example:
Carbon monoxide is emitted globally in large amounts and is toxic in high concentrations

The global emission rate of carbon monoxide (CO)

⇨ **2800 Tg per year**

Without removal (hypothetical):

Global CO concentrations would reach harmful levels (30 ppmv) in only 50 years

Example:
Carbon monoxide is emitted globally in large amounts and is toxic in high concentrations

The global emission rate of carbon monoxide (CO)

⇨ **2800 Tg per year**

The global CO concentration is nearly constant over time

⇨ **50 - 100 ppbv**

How is CO removed from the atmosphere ?

Physical Removal from the Atmosphere

- **Wet deposition**
  (washout by rain)

Water soluble components

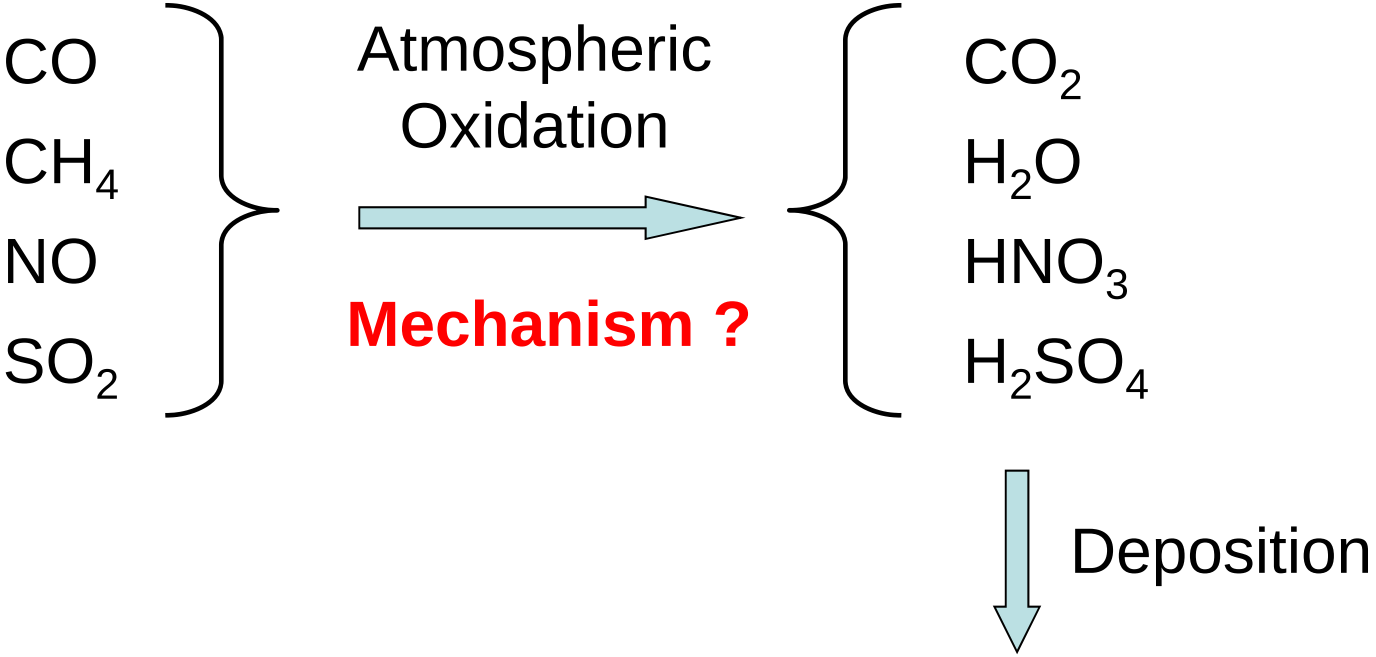
- **Dry deposition**
  (on vegetation, soil, ground...)

Sticky or reactive components

⇨ Inefficient for many emitted trace gases
CO, NOx, CH_4, Isoprene, other VOCs, CFCs ...

Chemical Removal from the Atmosphere

- Large **excess of oxygen** (21% O_2)
- Thermodynamics favours **atmospheric oxidation**



CO

CH_4

NO

SO_2

Atmospheric Oxidation

Mechanism ?

CO_2

H_2O

HNO_3

H_2SO_4

Deposition

Self Cleaning the Atmosphere by Hydroxyl Radicals (OH)

First proposed by H. Levy II, 1972

- **Ozone, water vapour and solar UV produce atmospheric OH**

$$\begin{aligned} \mathrm{O_3} + h\nu\ (<340\,\mathrm{nm}) &\rightarrow \mathrm{O(^1D)} + \mathrm{O_2} \\ \mathrm{O(^1D)} + \mathrm{H_2O} &\rightarrow \mathrm{OH} + \mathrm{OH} \end{aligned}$$

Self Cleaning the Atmosphere by OH

- OH reacts with most trace gases and initiates their chemical degradation

$$CO + OH \rightarrow CO_2 + H$$

$$CH_4 + OH \rightarrow CH_3 + H_2O \rightarrow \ldots \rightarrow CO_2 + H_2O$$

$$NO_2 + OH \xrightarrow{M} HNO_3$$

$$SO_2 + OH \xrightarrow{M} HSO_3 \rightarrow \ldots \rightarrow H_2SO_4$$

Self Cleaning the Atmosphere by OH

- The reaction with OH is the rate-determining step in the removal of atmospheric trace gases.

$$\tau_X = \frac{1}{k_{OH+X} \times [OH]}$$

natural (1/e)
chemical lifetime (s)
of compound X

bimolecular
rate coefficient
for X + OH → Prod.
(molecules^{-1}cm^{3} s^{-1})

OH number-density
concentration
(molecules cm^{-3})

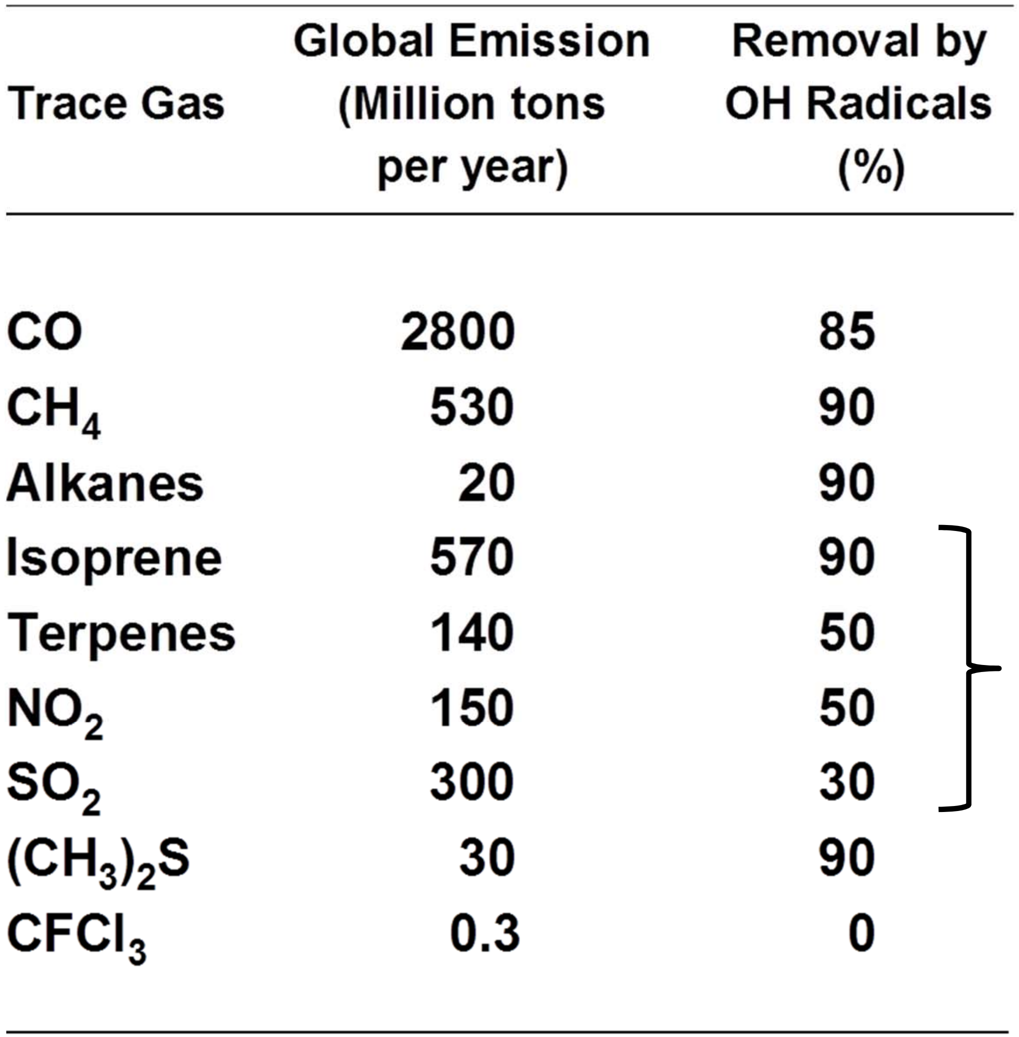
Atmospheric Lifetimes

Gas	Atmospheric lifetime	Transport distance within lifetime
NO_2	1 day	few hundred km
CO	2 months	global hemisphere
CH_4	8 years	global
CFC-11*	60 years	global
CFC-12 *	130 years	global

Global mean OH concentration ~ 10^6 molecules / cm^3

* Not attacked by OH

Removal of Trace Gases by OH

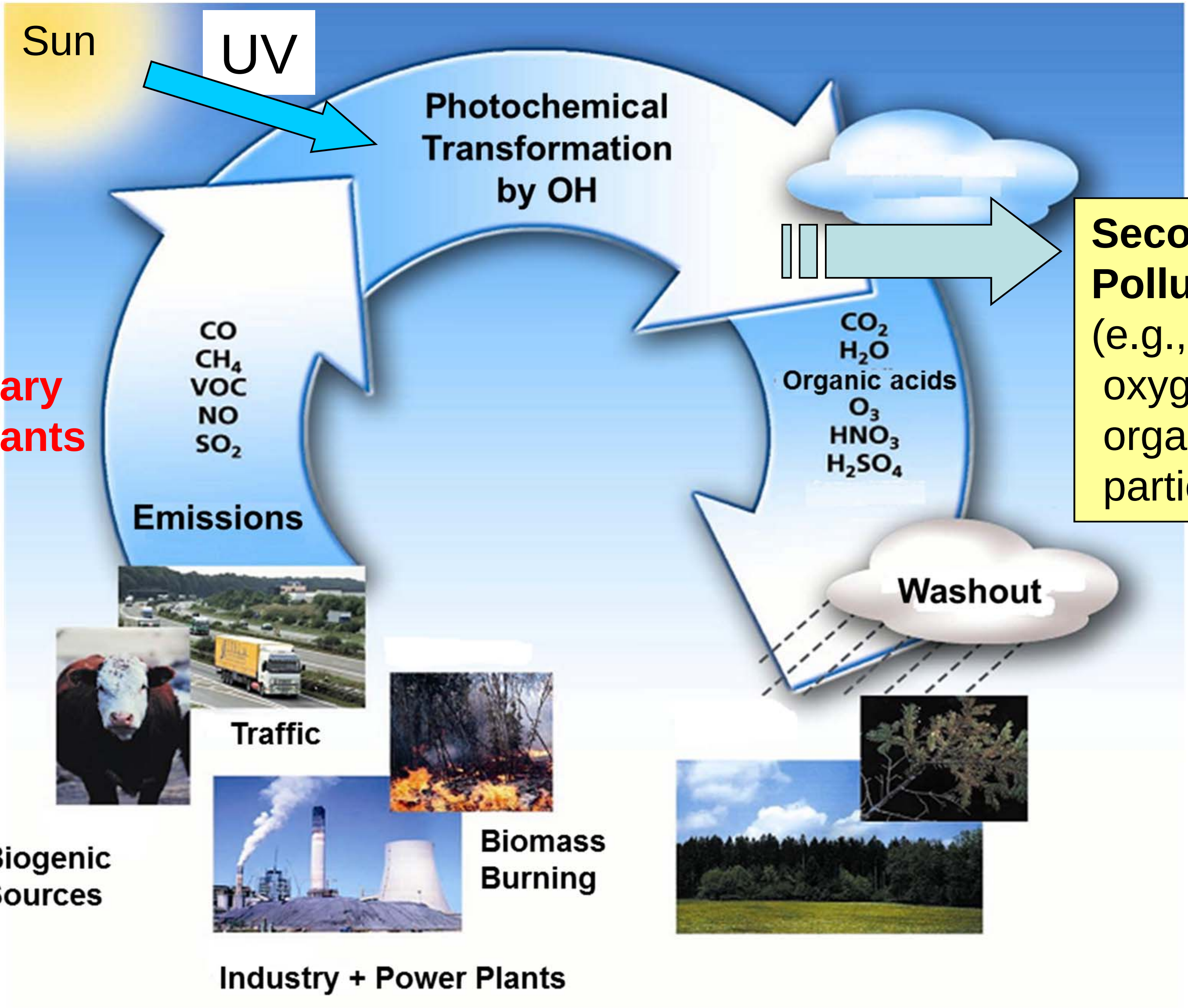


Trace Gas	Global Emission (Million tons per year)	Removal by OH Radicals (%)
CO	2800	85
CH_4	530	90
Alkanes	20	90
Isoprene	570	90
Terpenes	140	50
NO_2	150	50
SO_2	300	30
$(CH_3)_2S$	30	90
$CFCl_3$	0.3	0

Additional removal, e.g. by NO_3, O_3, Criegee radicals

after Ehhalt (1999)

Self Cleaning of the Atmosphere



Sun

UV

Primary Pollutants

Secondary Pollutants (e.g., ozone, oxygenated organics, particles)

If we want to understand atmospheric self-cleaning
and secondary pollutant formation,
we need to understand
atmospheric radical chemistry !

Primary Formation of OH Radicals

- Photodissociation of trace gases

$$\left.\begin{array}{lllllll} O_3 & + & h\nu\ (<340\mathrm{nm}) & \rightarrow & O(^1D) & + & O_2 \\ O(^1D) & + & H_2O & \rightarrow & OH & + & OH \end{array}\right\} \text{global}$$

$$HONO + h\nu\ (<400\mathrm{nm}) \rightarrow OH + NO$$

Nitrous acid

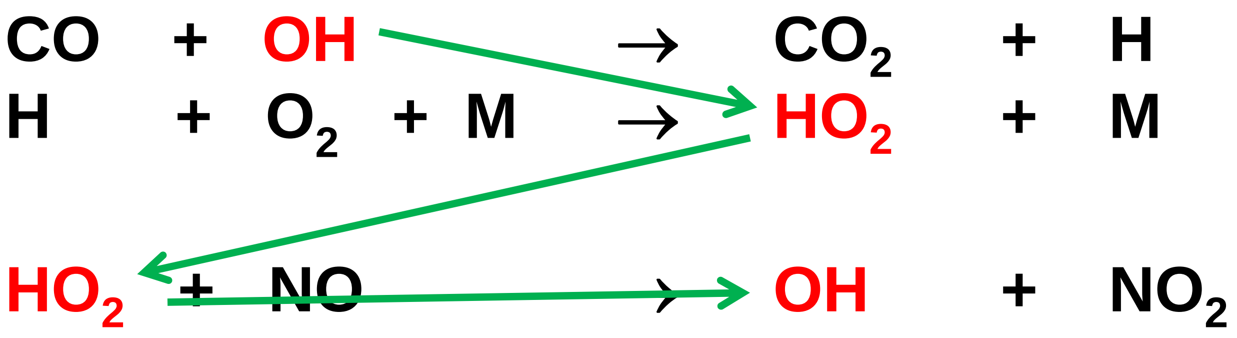
⇧

$$\left.\begin{array}{l} \text{Surface reactions} \\ \text{of } NO_2\text{, } HNO_3\text{, nitrates} \\ \text{on soil, organic material,} \\ \text{teflon, quartz, ...} \\ \text{(often enhanced by light)} \end{array}\right\} \text{continental}$$

Secondary Formation of OH Radicals

- OH production by recycling from HO_2 radicals

hydroperoxy radicals



$$CO + OH \rightarrow CO_2 + H$$

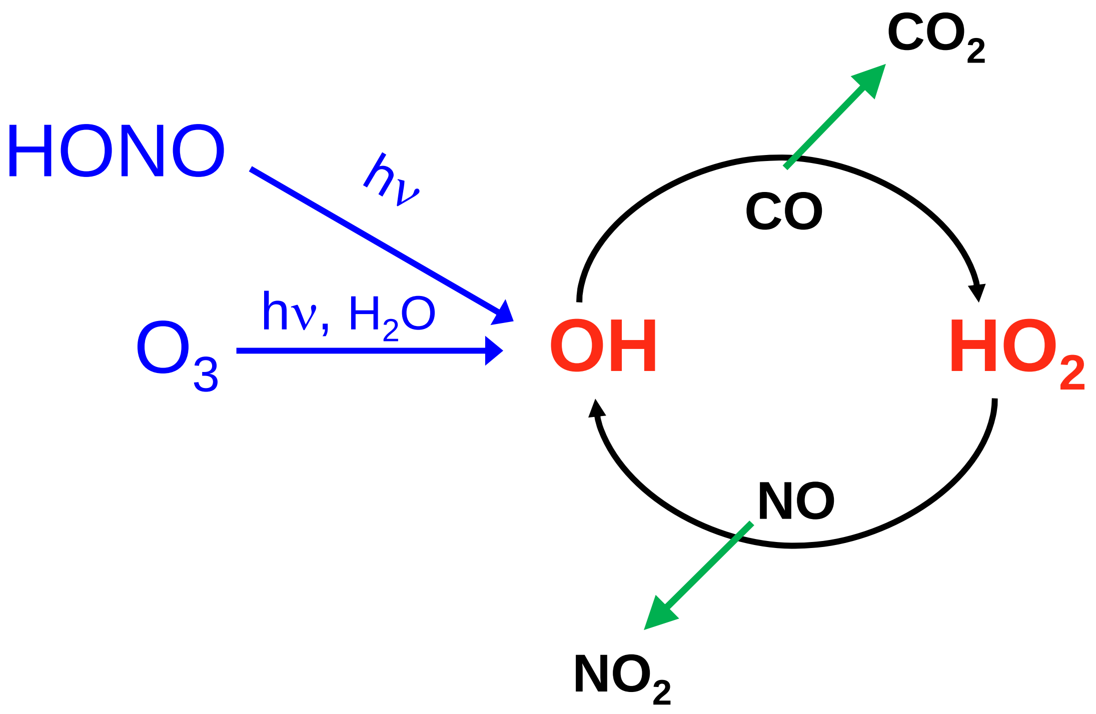
$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow OH + NO_2$$

Enhancement of the atmospheric oxidation efficiency by chain reactions

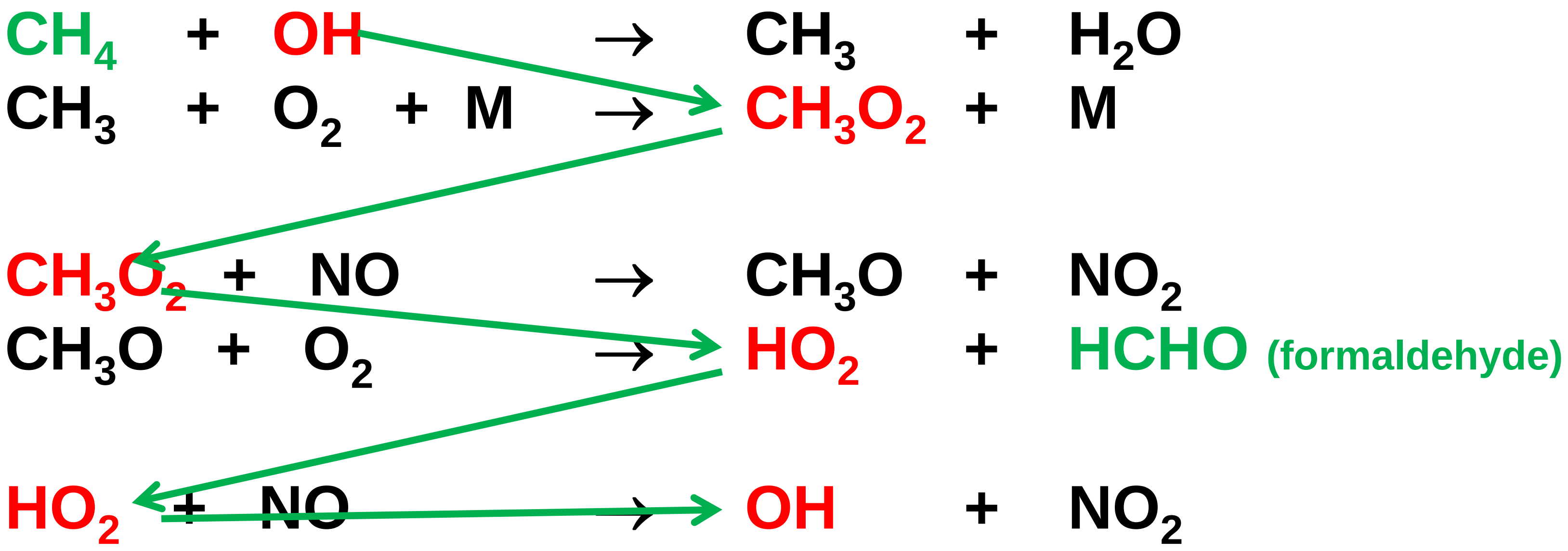
Simplified Chemistry Scheme

Radical chain reactions
with OH regeneration



Secondary Formation of OH Radicals

- OH regeneration in methane oxidation



$$CH_4 + OH \rightarrow CH_3 + H_2O$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$$

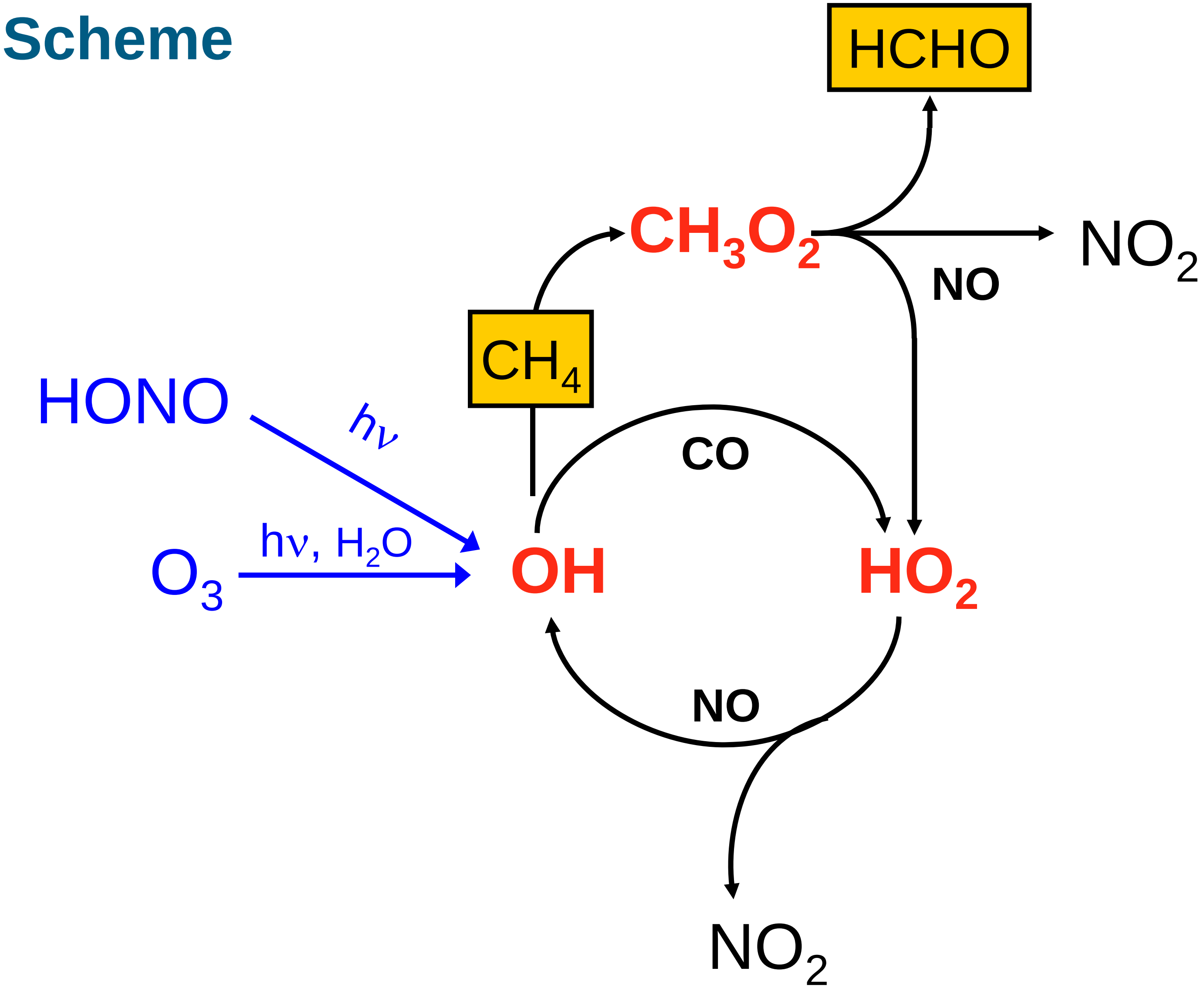
$$CH_3O_2 + NO \rightarrow CH_3O + NO_2$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO$$ (formaldehyde)

$$HO_2 + NO \rightarrow OH + NO_2$$

CH_3 = methyl radical
CH_3O_2 = methyl peroxy radical
CH_3O = methoxy radical

Simplified Chemistry Scheme



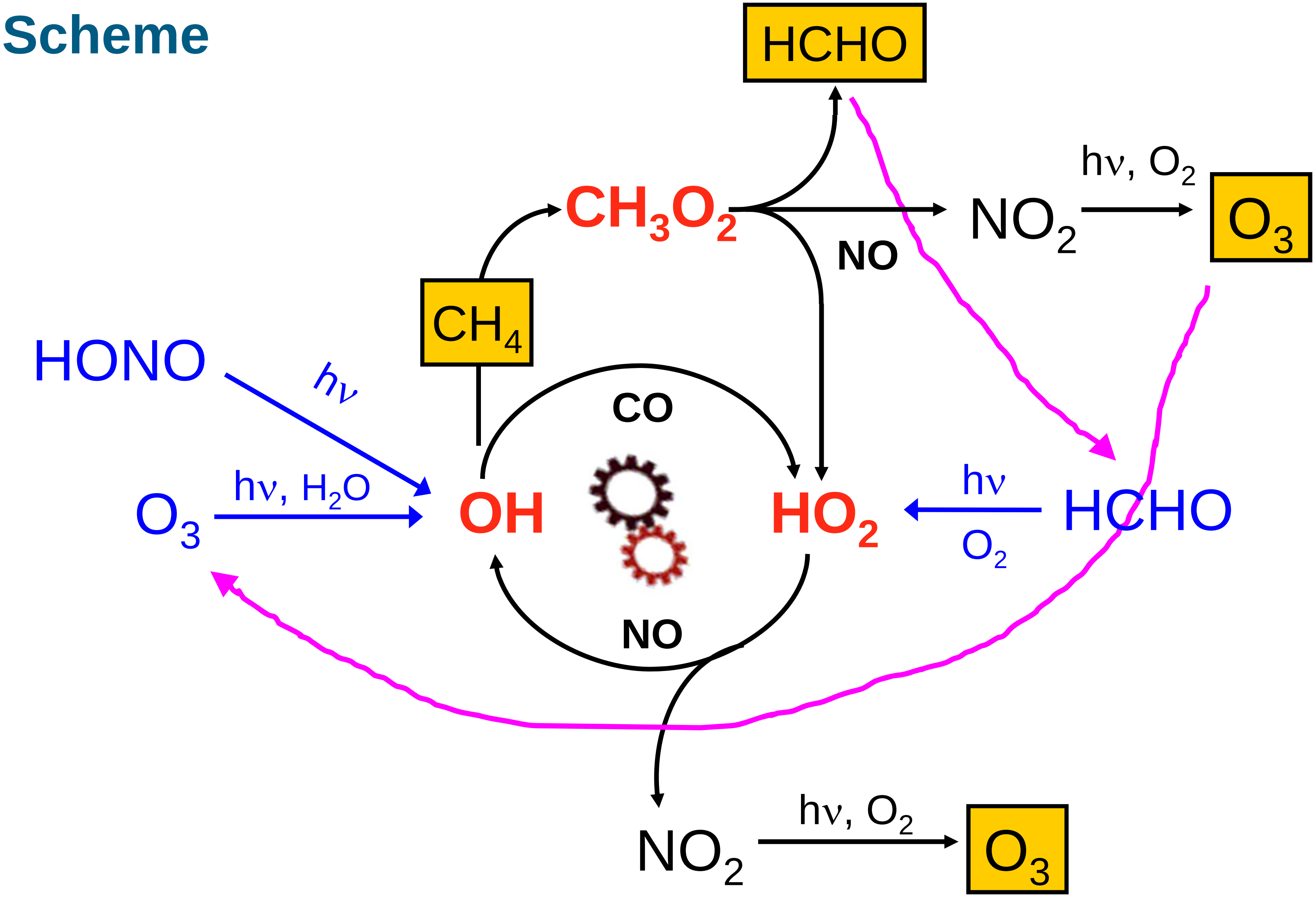
Photochemical Ozone Formation

$$NO_2 + h\nu\ (<400\,\text{nm}) \rightarrow NO + O$$

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

	Net ozone formation ?
$NO \xrightarrow{O_3} NO_2$	no
$NO \xrightarrow{HO_2,\ RO_2} NO_2$	yes
Emission $\longrightarrow NO_2$	yes

Simplified Chemistry Scheme



HCHO

$h\nu$, O_2

CH_3O_2

NO_2

O_3

NO

CH_4

HONO

$h\nu$

CO

O_3

$h\nu$, H_2O

OH

HO_2

$h\nu$

HCHO

O_2

NO

NO_2

$h\nu$, O_2

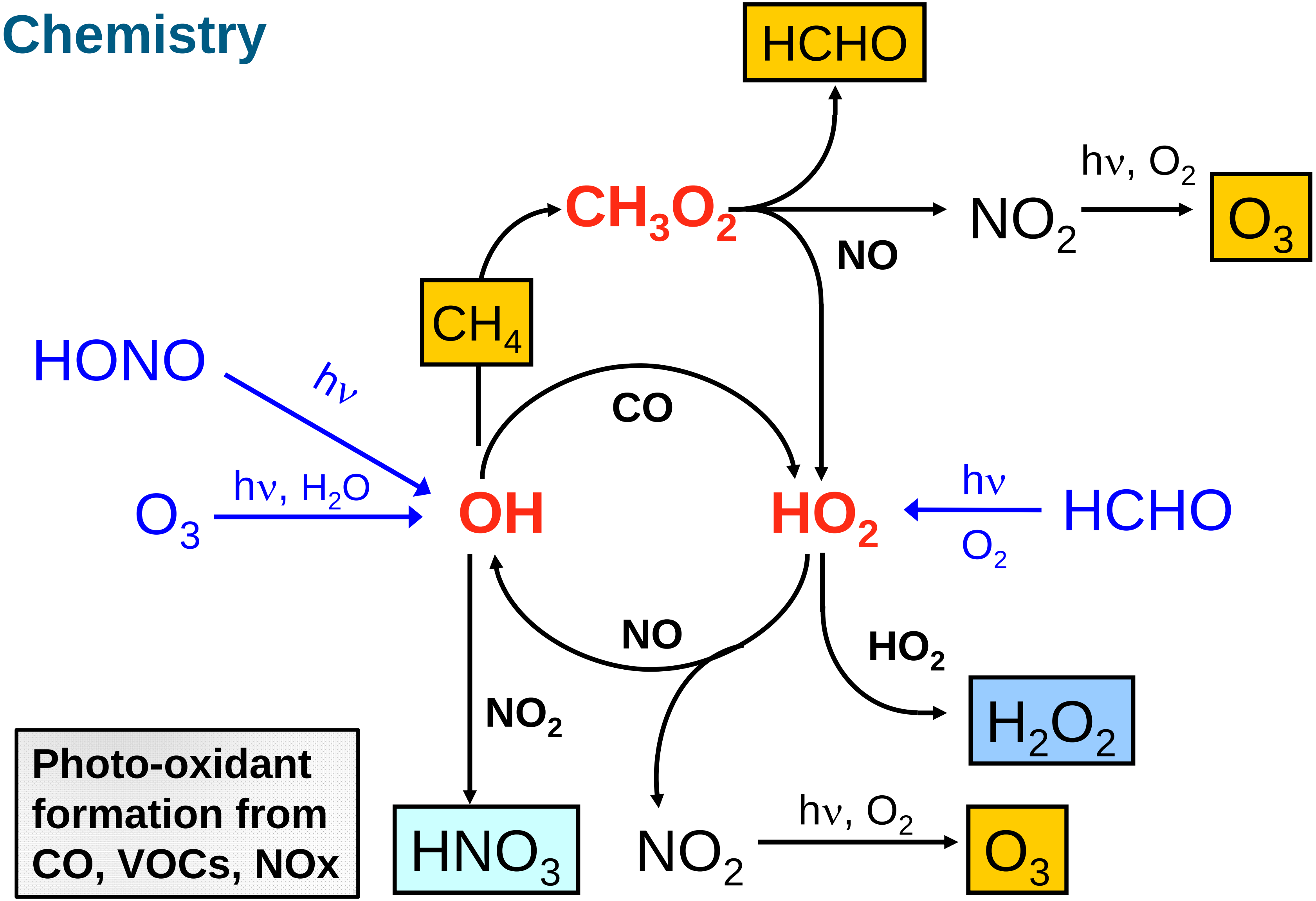
O_3

Radical Destruction

- Chain termination by radical self-reactions

$OH + NO_2 + M \rightarrow HNO_3 + M$	nitric acid
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	hydrogen peroxide
$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	methyl peroxide

Simplified Radical Chemistry



$HCHO$

CH_3O_2

$h\nu, O_2$

NO_2

O_3

NO

CH_4

$HONO$

$h\nu$

CO

O_3

$h\nu, H_2O$

OH

HO_2

$h\nu$

O_2

$HCHO$

NO

HO_2

NO_2

H_2O_2

HNO_3

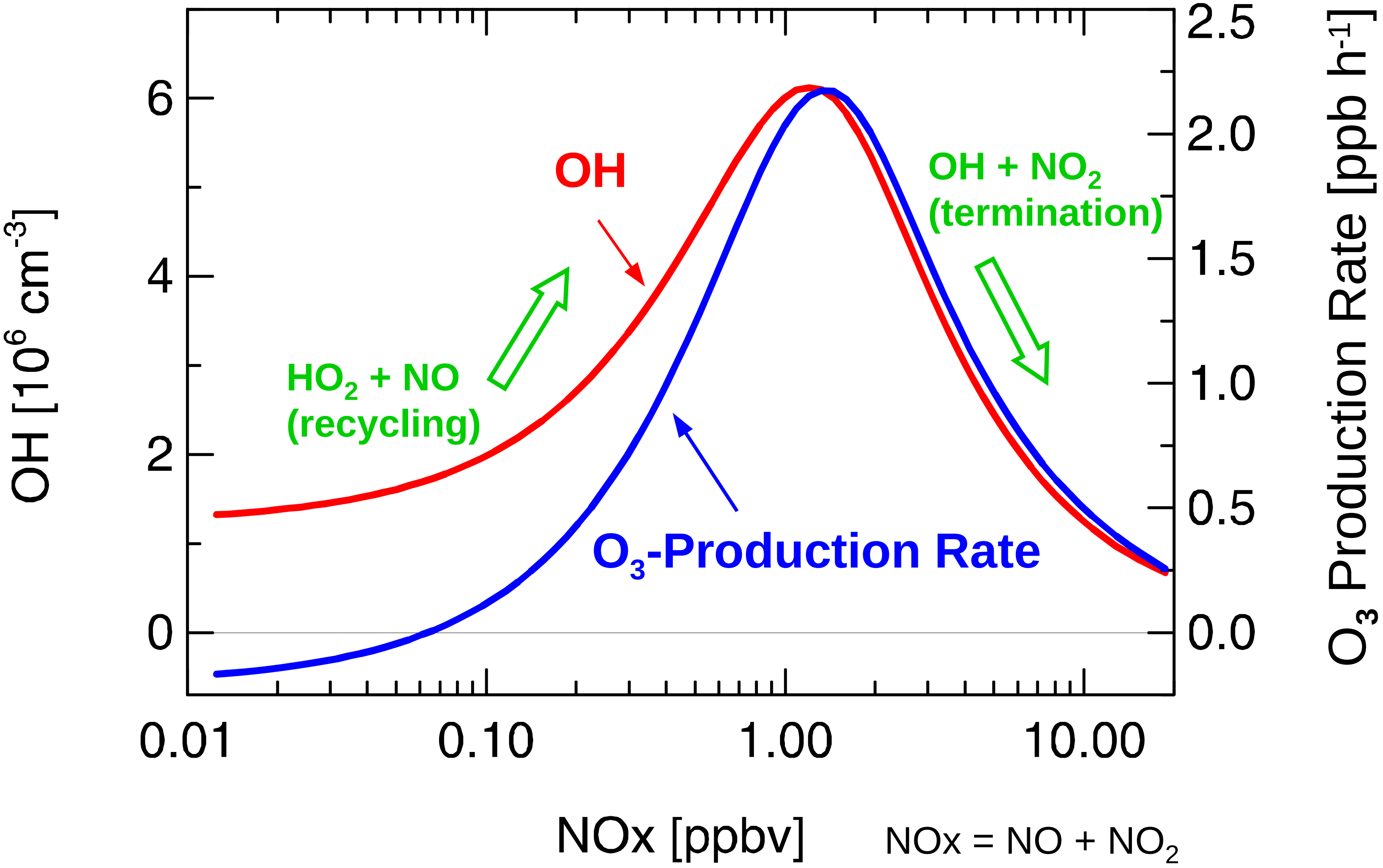
NO_2

$h\nu, O_2$

O_3

Photo-oxidant formation from CO, VOCs, NOx

OH Concentration and Ozone Production



NOx = NO + NO$_2$

Atmospheric Measurements of Radicals

How well do observations agree with theory ?

Laser Induced Fluorescence (LIF)

- Measurement of [OH]:

$OH + h\nu_{laser}$ (308 nm) $\longrightarrow$ OH^*

$OH^* \longrightarrow OH + h\nu$

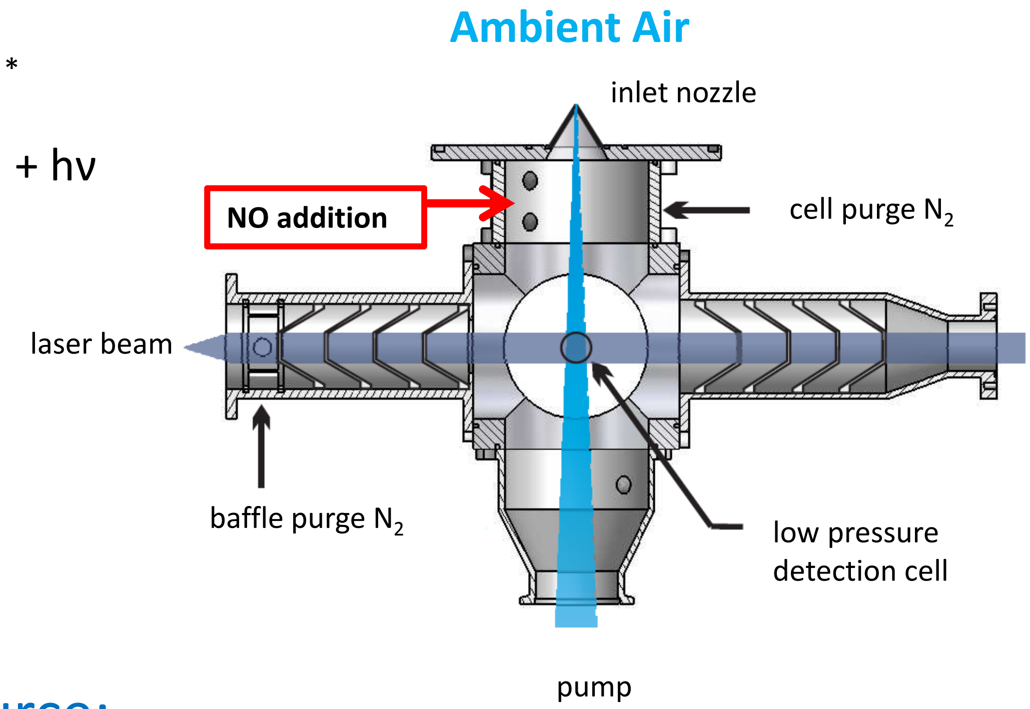
- Measurement of [HO_2]:

$HO_2 + NO \longrightarrow OH + NO_2$

- Calibration with radical source:

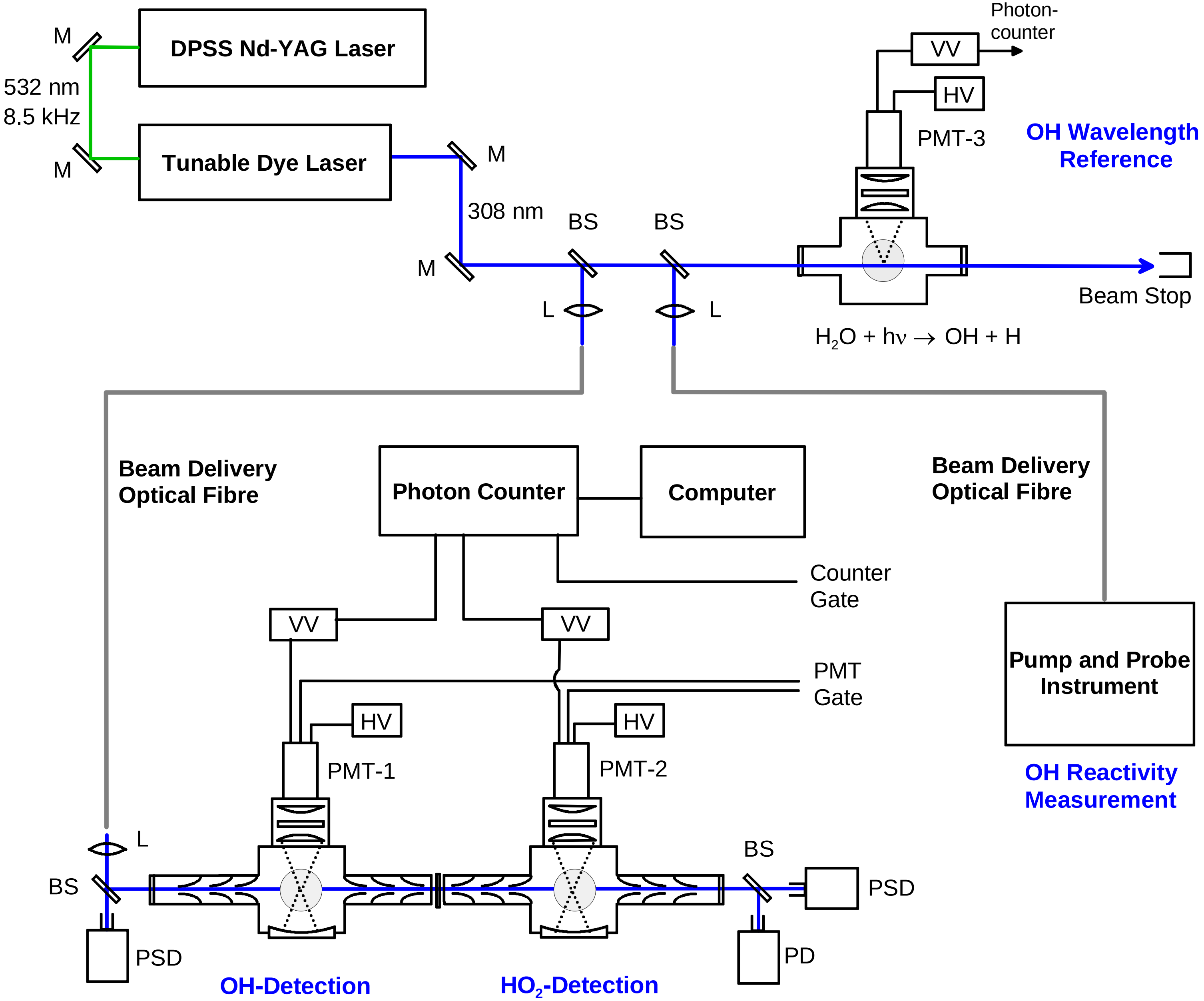
$H_2O + h\nu$ (185 nm) $\longrightarrow$ $OH + H$

$H + O_2 + M \longrightarrow HO_2 + M$



Mitglied der Helmholtz-Gemeinschaft

LIF Instrument



Deployment of Laser Induced Fluorescence (LIF) for OH and HO_2 Measurements

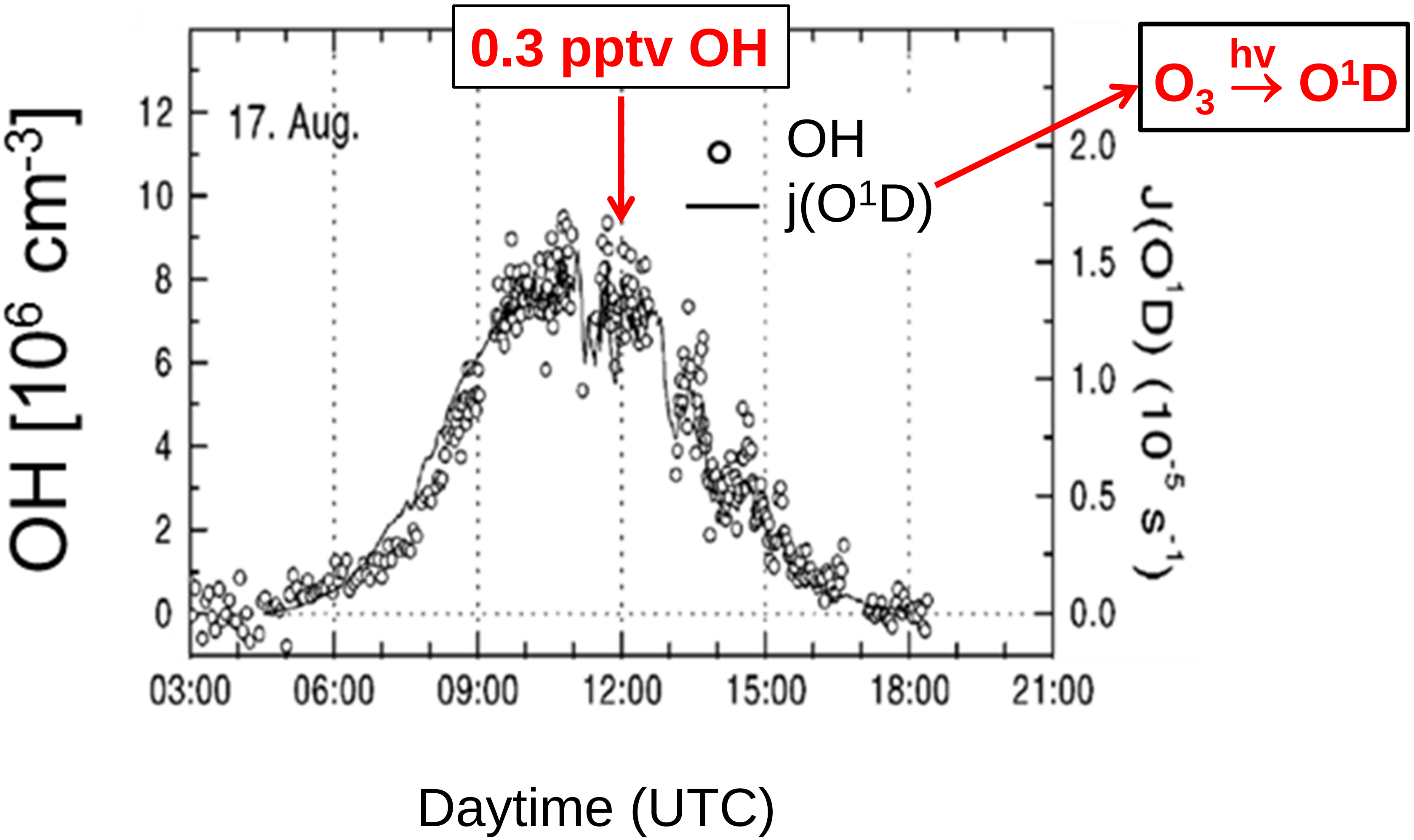

SAPHIR

Zeppelin NT


Pearl River Delta


HALO

OH Measurement by LIF in a Clean Atmosphere (North-East Germany)

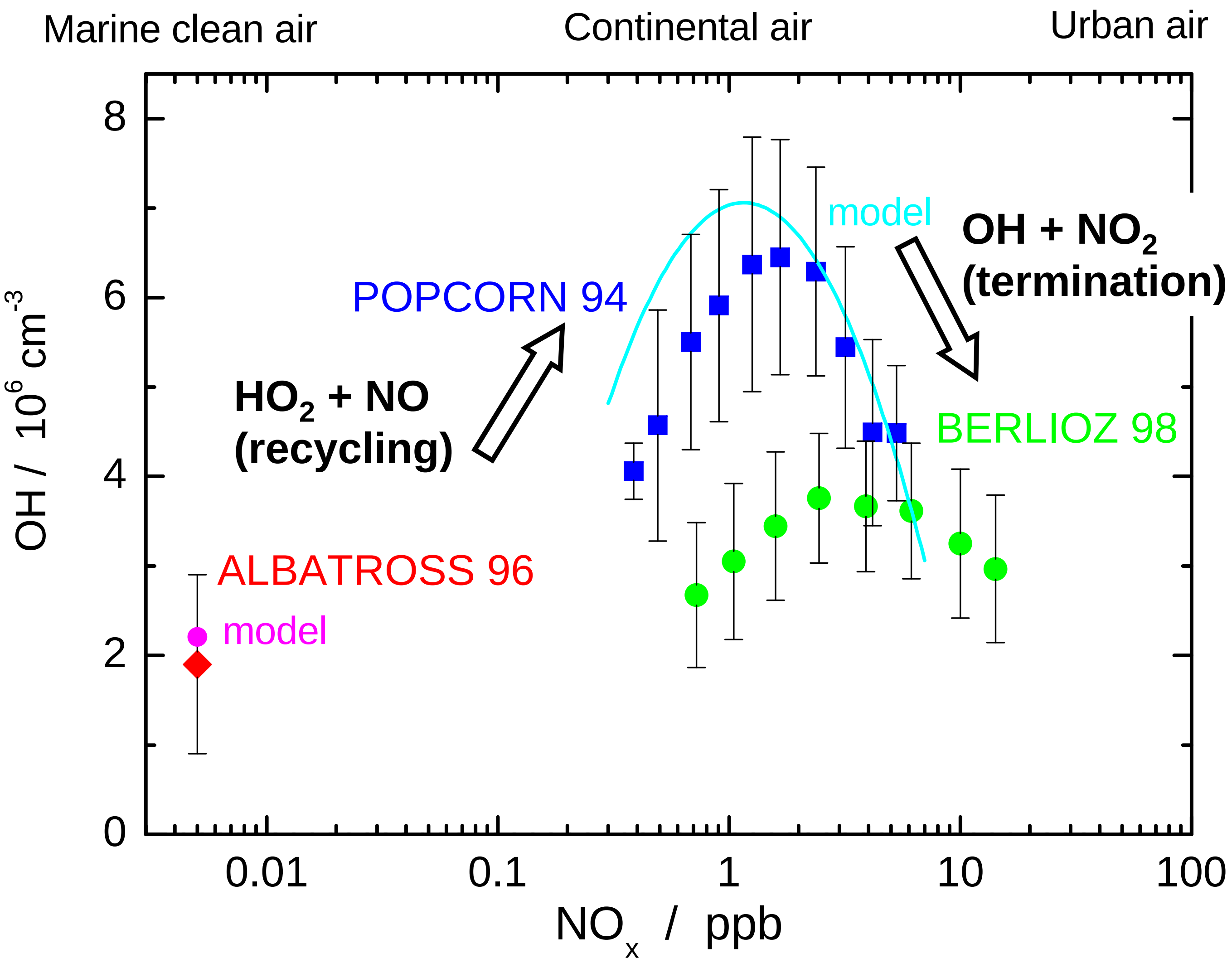


0.3 pptv OH

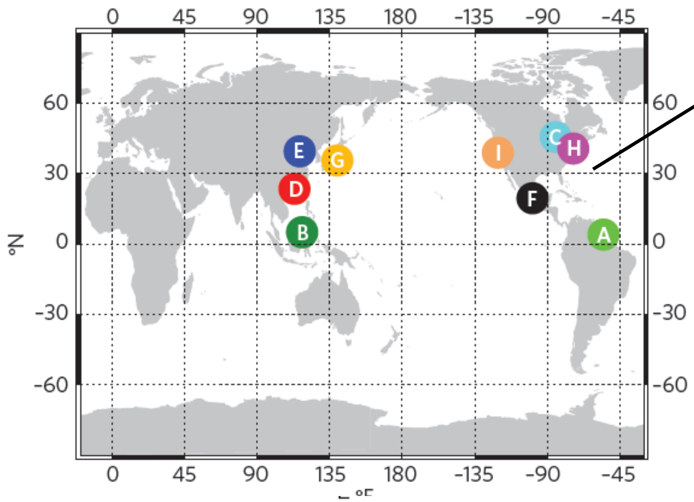
$O_3 \xrightarrow{hv} O^1D$

Holland et al. (1998)

OH observations in regions with low VOC concentrations

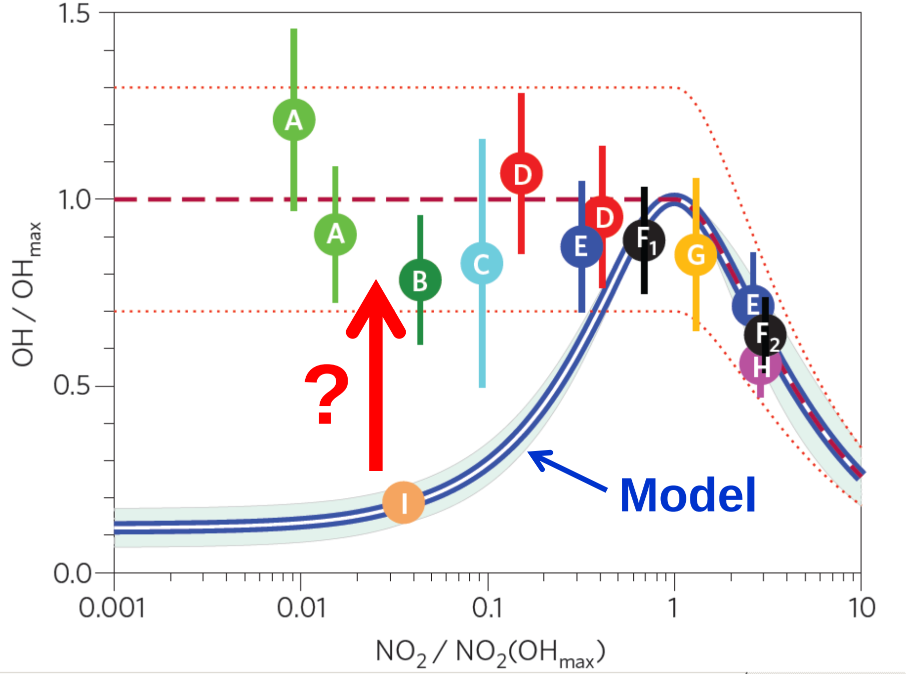


OH observations in regions with high VOC concentrations



Field campaigns ($k_{OH} > 10\ s^{-1}$)

A Lelieveld et al. 2008
B Whalley et al. 2011
C Tan et al. 2001
D Hofzumahaus et al. 2009
E Lu et al. 2013
F1 Mao et al. 2009
F2 Dusanter et al. 2009
G Kanaya et al. 2007
H Ren et al. 2003
I Mao et al. 2012



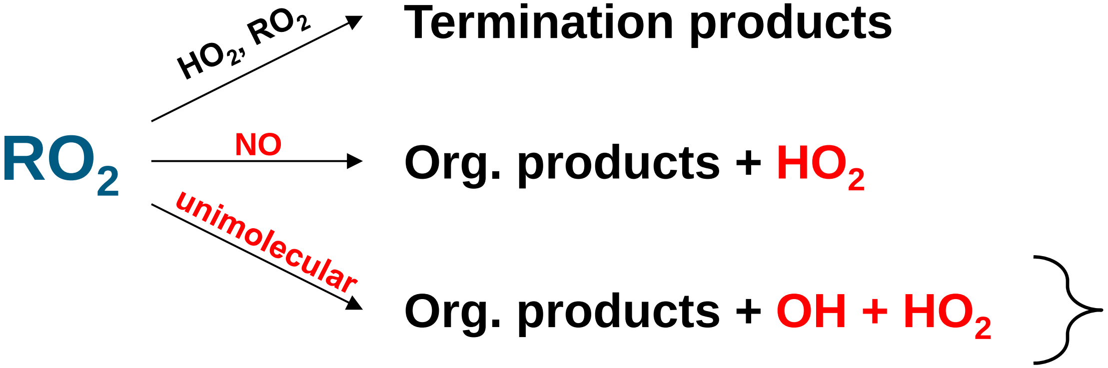
OH is significantly underpredicted at NO < 0.5 ppbv in biogenically influenced regions (e.g. forests)

Rohrer et al. Nature Geosci. 2014

Experiments in the atmosphere simulation chamber SAPHIR

Chamber
- Volume: 270 m^3
- Walls: Teflon film
- Light source: Solar radiation

Measurements
- OH, HO_2, RO_2, O_3, H_2O, CO, NO, NO_2, HONO, CH_4, VOCs
- Solar radiation, T, p



Termination products

Org. products + HO_2

Org. products + OH + HO_2

E.g. isoprene, methacrolein, monoterpenes

Newly discovered class of recycling reactions

Summary

Progress in understanding through field campaigns, laboratory + chamber experiments, theoretical calculations, and modelling

- OH radicals control the atmospheric self-cleaning.
- OH chemistry is relatively well understood in clean air
- OH chemistry is not well understood in environments with high VOC concentrations affecting:
  - atmospheric self-cleaning
  - photochemical production of ozone
  - formation of secondary organic aerosols