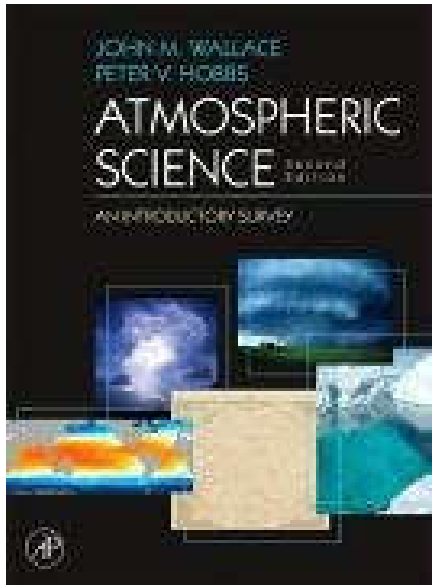
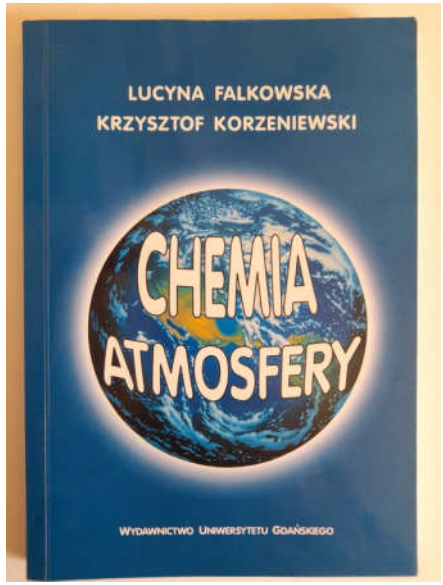
Atmosfera – chemia

Grzegorz Karwasz

Wykład 9

Thanks for a significant contribution to
prof. Daniela Ascenzi, Università di Trento



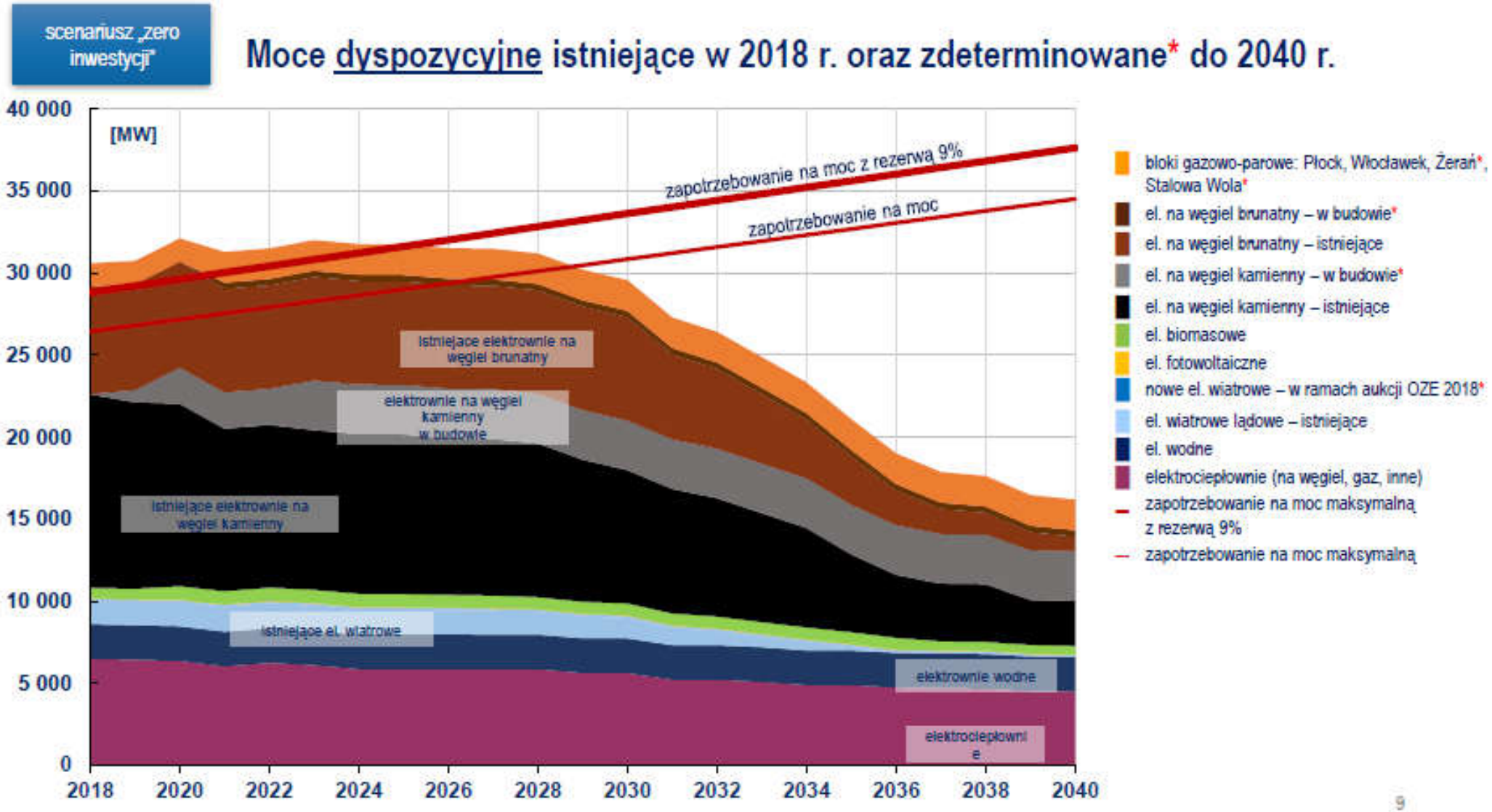


Najprawdopodobniej w 2033 roku zabraknie w Polsce 33% energii elektrycznej, a w 2044 roku stężenie CO_2 w atmosferze przekroczy 440 części na milion, przez co średnia temperatura na globie podniesie się o 1,4ºC.

Ale przypuszczalnie już w 2055 roku w Republice Korei uruchomiony zostanie przemysłowy reaktor termojądrowy (taki jak Słońce), a energii z niego (i jemu podobnych) wystarczy na ponad dwa i pół tysiąca lat.

Jak do tego dojdzie, i co ma z tym wszystkim wspólnego ogniwo (stos) Volty z 1799 roku, dowiemy się podczas wykładu

Polityka energetyczna Polski (ME, 22.01.2019)



https://www.gov.pl/web/energia/raport-mit-o-przyszlosci-energii-jadrowej

Rationale

Atmosphere Editorial Office
atmosphere@mdpi.com

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To Grzegorz Karwasz 12:42

Discover the Latest at Atmosphere (January 2025)

A Quick Look at the Atmospheric Circulation Leading to Extreme Weather Phenomena on a Continental Scale

Flavio Tiago Couto et al.

Read More »

Varying Performance of Low-Cost Sensors During Seasonal Smog Events in Moravian-Silesian Region

Václav Nevrlý et al.

Read More »

Population-Level Exposure to $PM_{2.5}$, NO_2,

Sources and Variability of Greenhouse Gases over Greece

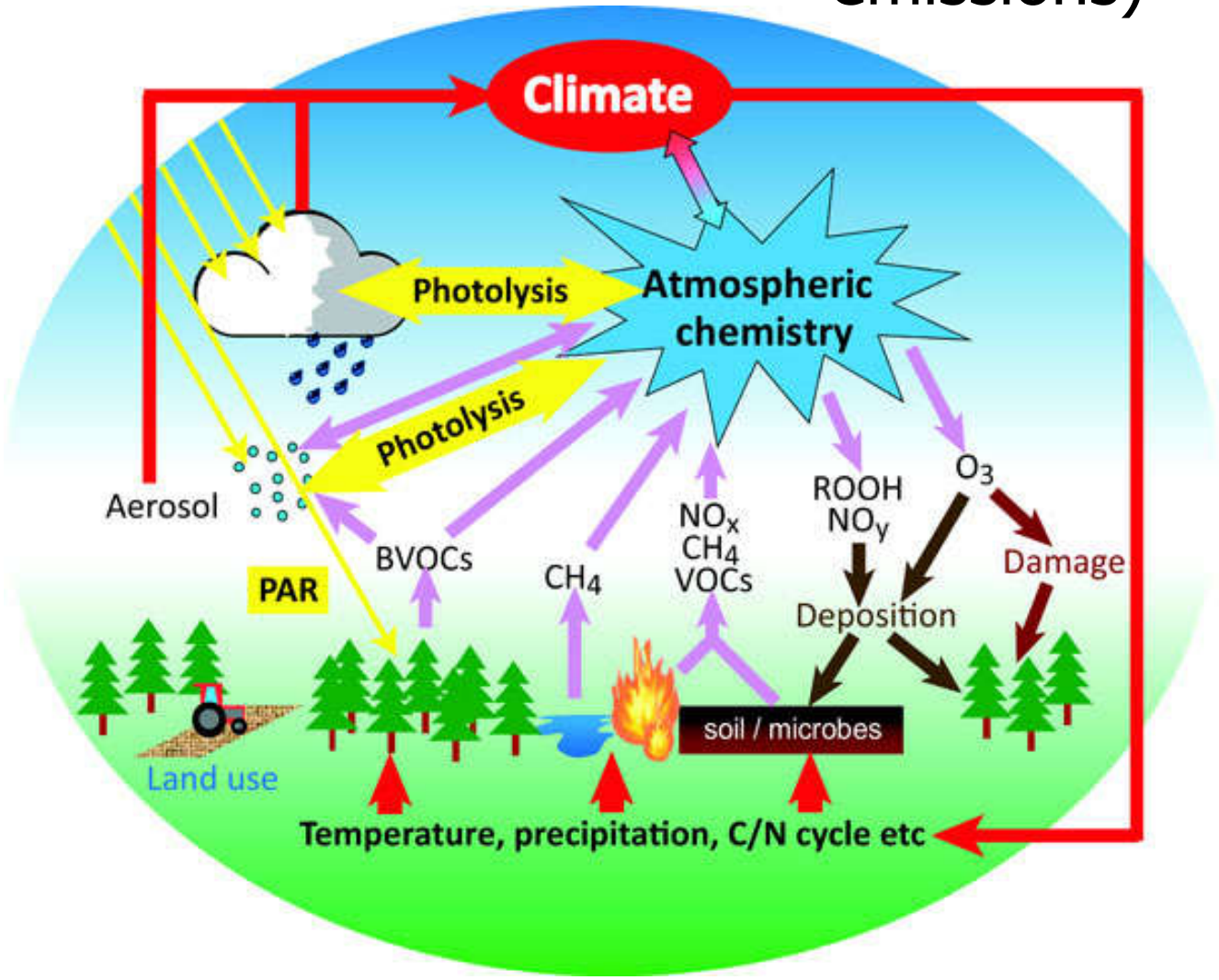
Environmental Physical Chemistry

Light/matter interaction and basic principles of spectroscopy

Daniela Ascenzi
Dept. Physics, University of Trento, Italy
e-mail: daniela.ascenzi@unitn.it

Goals of atmospheric chemistry

Atmospheric chemistry ***is influenced*** by processes occurring outside (Sun) and on Earth (natural and anthropogenic emissions)



Atmospheric chemistry has ***influences*** on:

- Living organisms (health & environmental issues)
- climate
- weather

Chemia atmosfery

- Chemia fizyczna atmosfery:
- Termodynamika chemiczna i kinetyka w fazie gazowej
- Zasady spektroskopii i fotochemii
- Termodynamika cieczy i roztworów
- Cząstki, aerozole i chmury (fizyczne i chemiczne)
- właściwości, procesy zarodkowania, powstawanie, wzrost...)
- Cykle bio-geo-chemiczne w atmosferze (C, N, O i S)
- Zanieczyszczenia atmosferyczne (właściwości, powstawanie, niszczenie)
- Oddziaływanie promieniowania ze związkami atmosferycznymi
- Efekt cieplarniany
- Atmosfery innych planet (słonecznych) i satelitów

Credits: Daniela Ascenzi

«Geodium», Torun, cztery ery Ziemi

1. Epoka Ognia
2. Era wody
3. Epoka lodowcowa
4. Wiek człowieka

Projekt: Grzegorz Karwasz, Lucjan Broniewicz, Anna Broniewicz, 2011

2 Ma:
First Hominins

230-66 Ma:
Non-avian dinosaurs

4550 Ma:
Formation of the Earth
Hominins
Mammals
Land plants
Animals
Multicellular life
Eukaryotes
Prokaryotes

c. 380 Ma:
First vertebrate land animals

4527 Ma:
Formation of the Moon

c. 540 Ma:
Cambrian explosion

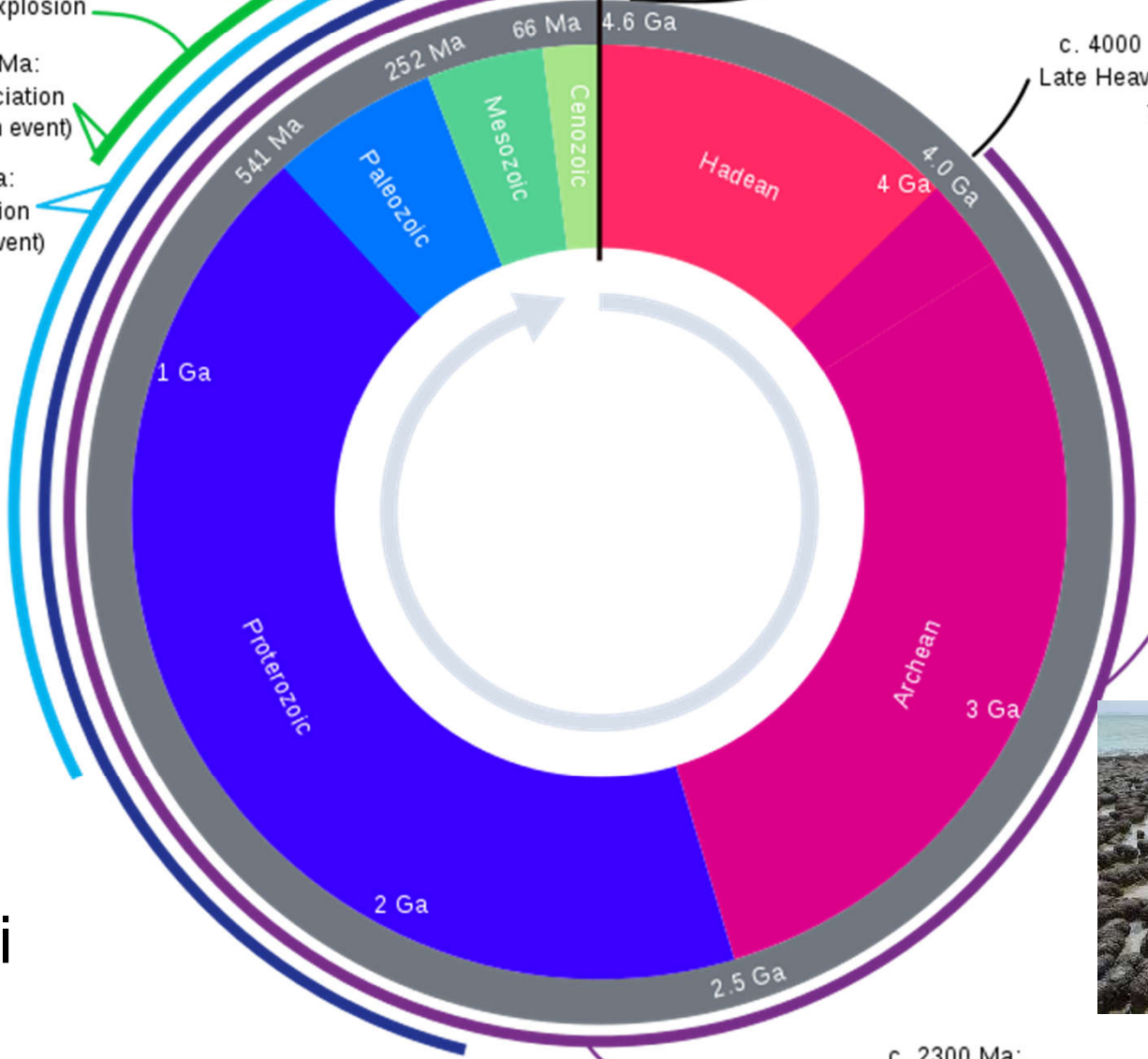
c. 650–635 Ma:
Marinoan Glaciation
(Snowball Earth event)

c. 716–660 Ma:
Sturtian Glaciation
(Snowball Earth event)

c. 4000 Ma: End of the
Late Heavy Bombardment;
first life

c. 3200 Ma:
Earliest start
of photosynthesis

c. 2300 Ma:
First major increase in atmospheric oxygen levels;
first Snowball Earth event (Huronian glaciation)

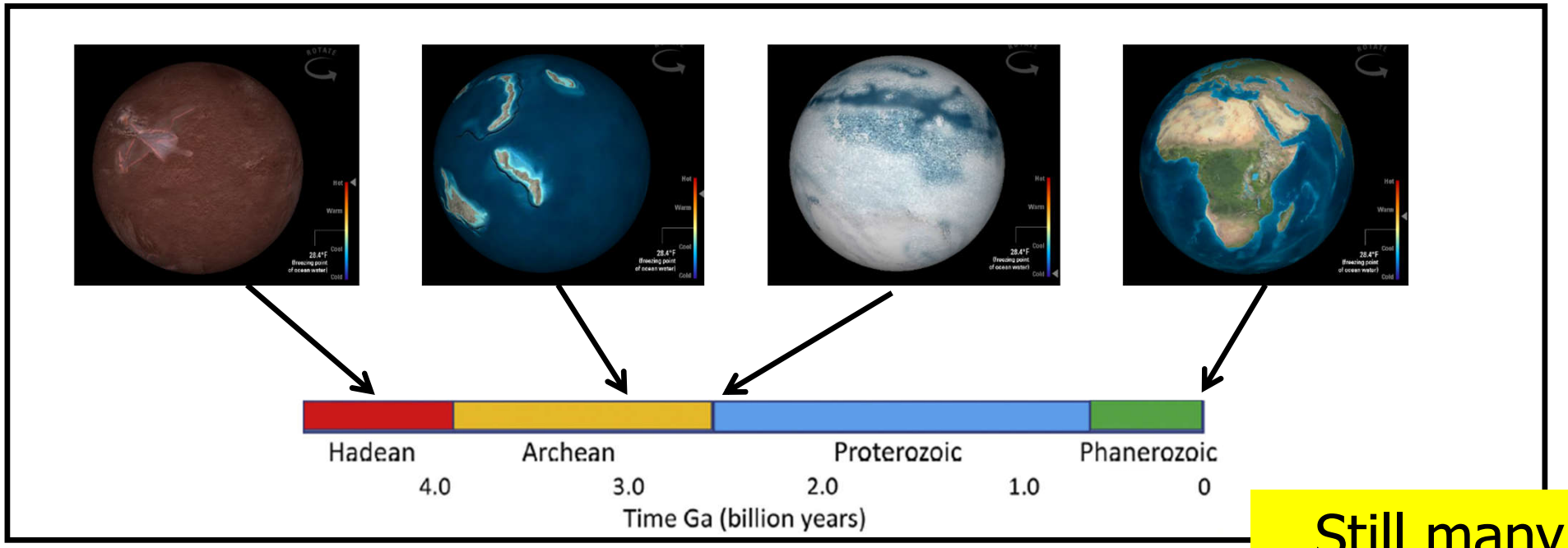


Eony Ziemi

https://en.wikipedia.org/wiki/Geologic_time_scale

Origin and evolution of the Earth's atmosphere

- Earth and the Solar system formed about 4.5 billion years ago
- Was the atmosphere the same from the beginning?
- What are the processes that led to the formation of an atmosphere?



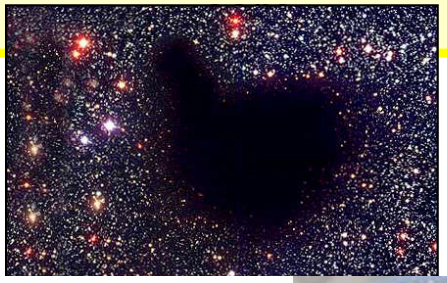
https://www.smithsonianmag.com/science-nature/travel-through-deep-time-interactive-earth-180952886/

Still many uncertainties

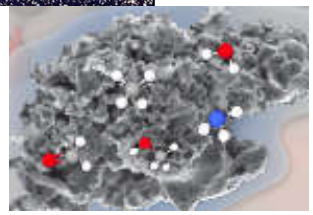
Formation of the Solar system

interstellar clouds:
~1% dust
~99% gas

STEP1: pre-stellar

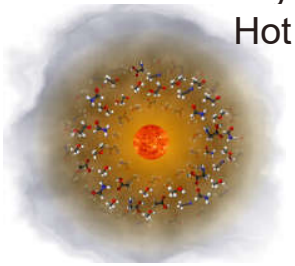


Size ~10^4 au
Duration ~ 10^5 yr
gas+dust → icy mantle formation

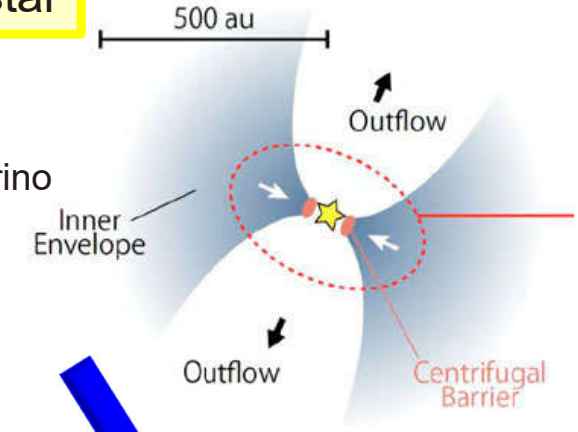


STEP2: protostar

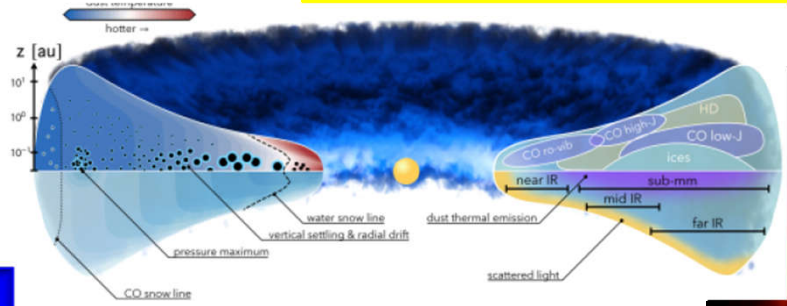
Size ~5-100 au
Duration ~ 10^4 yr?
Hot corino



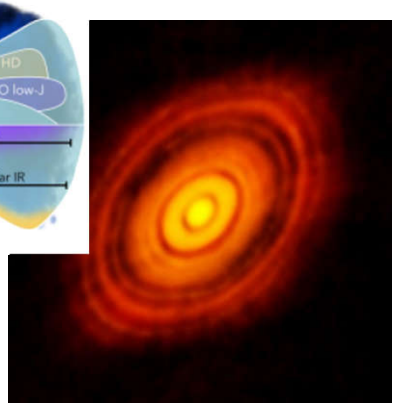
icy mantle sublimation



STEP3: protoplanetary disk



Size ~10-200 au
uration ~ 10^6 yr
Dust agglomeration



STEP4: planetary system

planets
comets
meteorites
asteroids

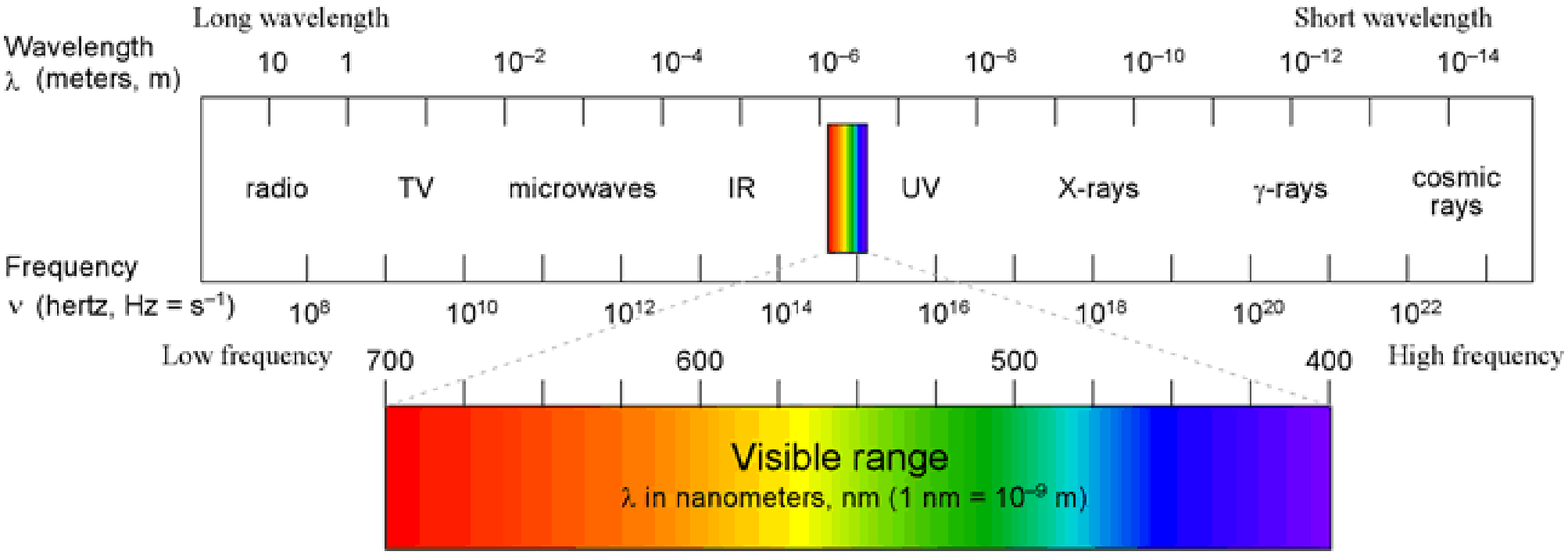
Small objects (planetesimals) accreted or combined together to build larger opjects (planets)

Differentiation of the Earth

- Early Earth was mostly molten («liquid rock») due to high temperatures (heat released from the accretion process and radioactive decay)
- Formation of Earth in a great part ocured in a (cosmologically) very short time – 10 mln years
- About 100 mln years after the beginning of the formation a catastrophic event happened: and object of the dimensions of Mars collided with young Earth. We have to „remnants" of this event: a relatively great Moon (that formed in 24 hours) and an inclined axis of rotation.
- Oxygen in the atmosphere appeared very late: for 1-2 bilion years cyano-bacteries produced it via photosynthesis from CO_2 , but the intitial amount has been burried as iron ores FeO_2 (like on Mars). When iron (in the crust) has been finished, the rest of O_2 went to atmosphere.

differentiation of the Early earth
https://www.youtube.com/watch?v=YKM6xhBK738
https://www.slideshare.net/KhanImran5975/how-did-atmosphere-form
https://pages.uoregon.edu/drt/Classes/201_99/Rice/differentiation.html

Light - The electromagnetic spectrum



Spektroskopia

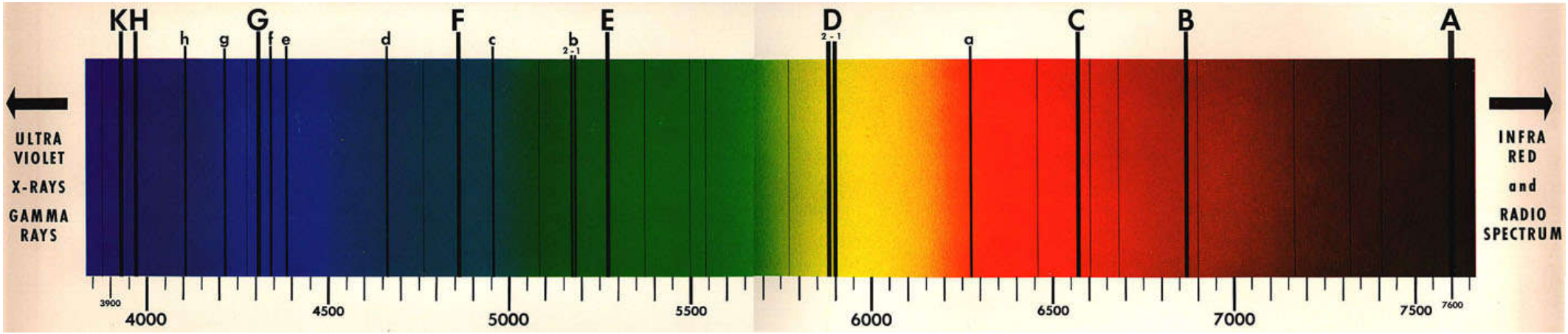
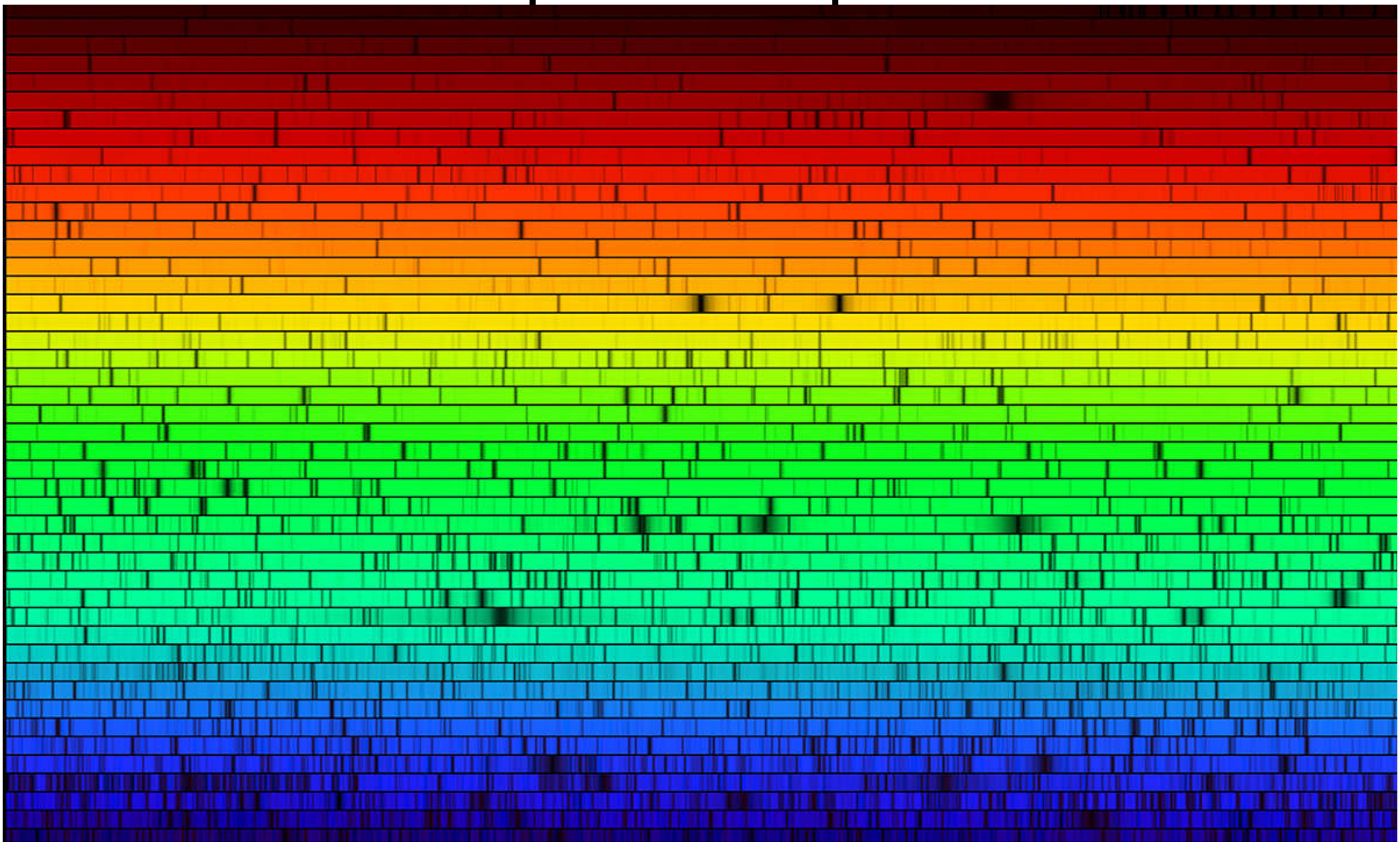


Table 1 -- "Known" Lines		
Designation	**Wavelength (Angstrom)**	**Origin**
A	7594	terrestrial oxygen
B	6867	terrestrial oxygen
C	6563	hydrogen (Hα)
D_1	5896	neutral sodium (Na I)
D_2	5890	neutral sodium (Na I)
E	5270	neutral iron (Fe I)
F	4861	hydrogen (Hβ)
H	3968	ionized calcium (Ca II)
K	3934	ionized calcium (Ca II)

https://www.columbia.edu/~vjd1/Solar%20Spectrum%20Ex.html

Spektroskopia



Fourier Transform Spectrometer at the McMath-Pierce Solar Facility at the National Solar Observatory on Kitt Peak, near Tucson, Arizona. https://science.nasa.gov/resource/the-solar-spectrum/

Skład atmosfery

Tablica 3.2

Składniki powietrza suchego (na podstawie Iribarne'a, Cho 1988)

Lp.	Nazwa gazu	Symbol	Udział procentowy objętościowy			Szacowany czas przebywania w atmosferze
Składniki główne						
1	Azot	N_2	78,09	99%	99.97%	$2 \cdot 10^7$ lat
2	Tlen	O_2	20,95			
3	Argon	Ar	0,93			
4	Dwutlenek węgla	CO_2	od 0 do 0,033			5 ÷10 lat
Składniki drugorzędne						
	Niezmienne		koncentracja			
5	Neon	Ne	18 ppm			$3 \cdot 10^6$ lat
6	Hel	He	5 ppm			
7	Krypton	Kr	1 ppm			
8	Ksenon	Xe	0,09 ppm			
9	Metan	CH_4	1,5 ppm			3 lata
10	Tlenek węgla	CO	0,1 ppm			0,35 lat
11	Wodór	H_2	0,5 ppm			
12	Podtlenek azotu	N_2O	0,25 ppm			< 200 lat

trwałe

półtrwałe

Skład atmosfery (2)

Zmienne			Typowa koncentracja		
13	Ozon	O_3	do 10 ppm w stratosferze 5—50 ppb (w powietrzu czystym), do 500 ppb w powietrzu zanieczyszczonym, przy gruncie	zmienne	
14	Siarkowodór	H_2S	0,2 ppb (nad lądem)		10 dni
15	Dwutlenek siarki	SO_2	0,2 ppb (nad lądem)		5 dni
16	Amoniak	NH_3	6 ppb (nad lądem)		1÷4 dni
17	Dwutlenek azotu	NO_2	1 ppb (nad lądem) 100 ppb w powietrzu zanieczyszczonym		2÷8 dni
18	Aldehyd mrówkowy	CH_2O	0 ÷ 10 ppb		

Elżbieta Wołoszczyn, *Meteorologia i klimatologia w zarysie*, PG, 2009

Atmosfera Ziemi

Table 5.1 Some gases in dry tropospheric air at a pressure of 1 atm

Gas	Chemical formula	Fraction of volume of air occupied by the species[a]	Residence time (or lifetime)[b]
Nitrogen	N_2	78.084%	1.6×10^7 years
Oxygen	O_2	20.946%	3000–4000 years
Argon	Ar	0.934%	—
Carbon dioxide	CO_2	379 ppmv[c]	3–4 years[d]
Neon	Ne	18.18 ppmv	—
Helium	He	5.24 ppmv	—
Methane[e]	CH_4	1.7 ppmv	9 years
Hydrogen	H_2	0.56 ppmv	~2 years
Nitrous oxide	N_2O	0.31 ppmv	150 years

Atmospheric Science, str. 155

Atmosfera Ziemi (c.d.)

Ozone	O_3	10–100 ppbv	Days–weeks
Nonmethane hydrocarbons (NMHC)[e]	–	5–20 ppbv	Variable
Halocarbons	–	3.8 ppbv	Variable
Hydrogen peroxide	H_2O_2	0.1–10 ppbv	1 day
Formaldehyde	HCHO	0.1–1 ppbv	~1.5 h
Nitrogen species ($NO + NO_2$ ($= NO_X$) $+ NO_3 + N_2O_5 + HNO_3 + PAN$)	NO_y	10 pptv–1 ppmv	Variable
Ammonia	NH_3	10 pptv–1 ppbv	2–10 days
Sulfur dioxide	SO_2	10 pptv–1 ppbv	Days
Dimethyl sulfide (DMS)	CH_3SCH_3	10–100 pptv	0.7 days
Hydrogen sulfide	H_2S	5–500 pptv	1–5 days
Carbon disulfide	CS_2	1–300 pptv	~120 h
Hydroxyl radical[f]	OH	0–0.4 pptv	~1 s
Hydroperoxyl radical[f]	HO_2	0–5 pptv	–

Importance of spectroscopy & photochemistry

1. Most chemical processes in the atmosphere are initiated by light

- photolysis of O_3 generates OH, the most important atmospheric oxidizer $O_3 + h\nu \rightarrow O_2 + O(^1D)$
  $O(^1D) + H_2O \rightarrow 2\ OH$
- solar photodissociation of many atmospheric molecules is often much faster than any other chemical reactions involving them. Some examples:

$CF_2Cl_2 + hv \rightarrow CF_2Cl + Cl$	(photolysis of CFCs in the stratosphere)
$HONO + hv \rightarrow OH + NO$	(source of OH in the troposphere)
$NO_2 + hv \rightarrow O + NO$	(source of O_3 in the troposphere)
$NO_3 + hv \rightarrow O_2 + NO$ or $O + NO_2$	(removal of NO_3 generated at night)
$Cl_2 + hv \rightarrow Cl + Cl$	(source of Cl atoms)
$H_2CO + hv \rightarrow H_2 + CO$ or $H + HCO$	(important step of hydrocarbon oxidation)

Importance of spectroscopy & photochemistry

2. Absorption of solar (and Earth) radiation by molecules directly influences the Earth energy balance

- grenhouse effect (CO_2, H_2O, N_2O, CFCs)
- stratospheric temperature inversion (O_3 photochemistry)

3. Spectroscopy of atmospheric molecules is used to detect them in situ

- OH is detected via an electronic transition (at 310 nm)
- NH_3 is detected via its fundamental vibrational transition at 1065 cm^{-1}
- ....

Types of radiation important in lower atmosphere

UV and visible radiation (λ=100-800 nm)

- excites bonding electrons in molecules
- capable of breaking bonds in molecules ($\rightarrow$ photodissociation)
- UV photons (λ=100-300 nm) have most energy, can break stronger bonds

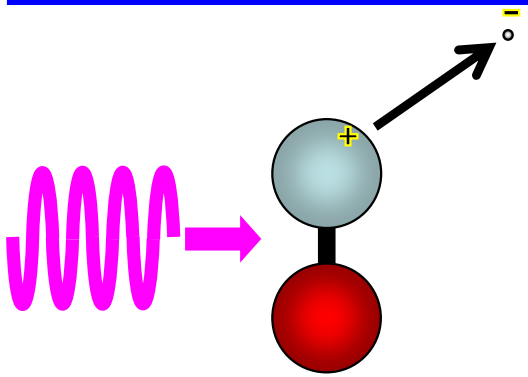
IR radiation (λ=0.8 - 300 μm)

- excites vibrational motions in molecules
- With very few exceptions IR is not energetic enough to break bonds and initiate photochemical processes

MW radiation (λ = 0.5 - 300 mm)

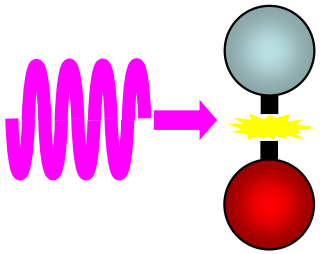
- excites rotational motions in molecules

Photophysical and chemical processes



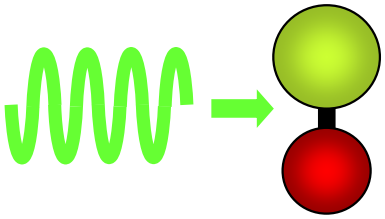
photoionization
(e^- emission)

UV-VIS and UV



photodissociation
(bond breaking)

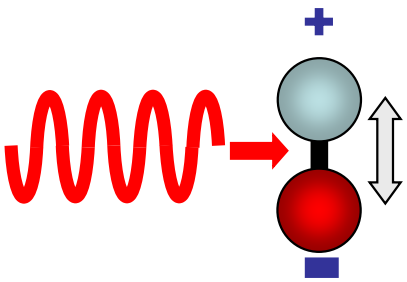
UV-VIS



electronic
excitation

visible (VIS)

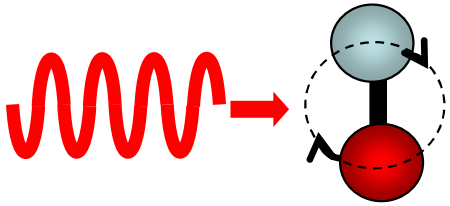
1.8-3.6 (eV))



vibration

infrared (IR)

100 meV



rotation 10 meV

microwaves

energy ($h\nu$)

Photochemical processes

Several important chemical processes in the atmosphere are initiated by light absorption

Example 1

VIS-UV light

radicals

$NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow NO^{\bullet} + O^{\bullet}$

$O^{\bullet} + O_2 + M \rightarrow O_3$

photochemical smog

Example 2

UV light

$O_3 + h\nu\ (\lambda < 336\ nm) \rightarrow O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow 2OH^{\bullet}$

Major source of OH (primary oxidant for organics, VOC)

Photon energies and bond dissociation energies

One mole of photons in the near UV (λ =320 nm) carries an energy of 374 kJ mol^{-1} (see exercise 2)
(1 eV = 96.5 kJ/ mol)

This energy is sufficient to break:

- weak chemical bonds (e.g. O_2-O in ozone ~100kJ/mol)

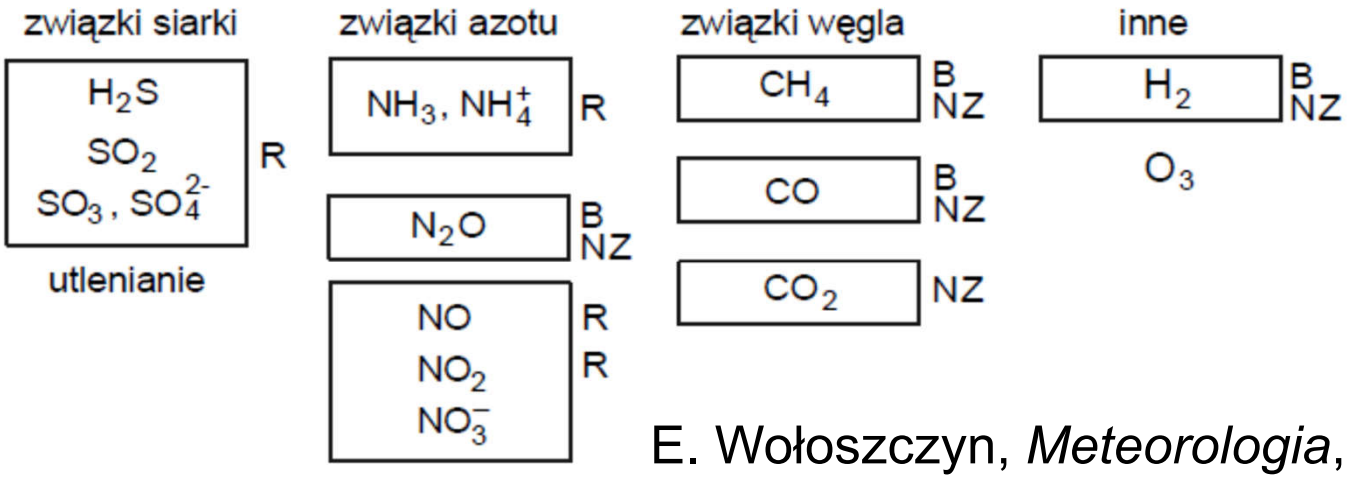
  $O_3 + h\nu\ (\lambda < 336\ nm) \rightarrow O(^1D) + O_2$

- moderately strong C-H bonds (e.g. formaldehyde ~368 kJ/mol)

Związki o znaczeniu chemicznym

Tablica 3.6

Związki o dużym znaczeniu dla chemii atmosfery



E. Wołoszczyn, *Meteorologia*, PG, 2009

Ramki oznaczają związki uczestniczące w tym samym obiegu.
R – reagujący: obieg związany z obiegiem wody, krótki τ, zmienny;
B – pochodzenie głównie biologiczne;
NZ – o stężeniu niezmiennym (półtrwały).

RESEARCH ARTICLE | DECEMBER 31 2019

Cross Sections for Electron Collisions with NO, N_2O, and NO_2

Mi-Young Song; Jung-Sik Yoon; Hyuck Cho; Grzegorz P. Karwasz; Viatcheslav Kokoouline; Yoshiharu Nakamura; Jonathan Tennyson

Check for updates

+ Author & Article Information

J. Phys. Chem. Ref. Data 48, 043104 (2019)

https://doi.org/10.1063/1.5114722 **Article history**

Reakcje chemiczne: cząsteczki, jony, rodniki

Rodnik – atom, cząsteczka, fragment cząsteczki z *niesparowanym* elektronem: stąd ogromna reaktywność rodników

$H_2O + h\nu \rightarrow OH^{\bullet} + H$ (fotoliza, powstanie rodnika)

$O_3 + h\nu \ (\lambda < 315\ nm) \rightarrow O^{*} + O_2$ (fotoliza ozonu, atom tlen w stanie wzbudzonym – metastabilnym)

$O^{*} + H_2O \rightarrow 2\ OH^{\bullet}$ (de-ekscytacja O^{*} , dysocjacja H_2O na rodniki $OH^{\bullet}$)

$CH_4 + OH^{\bullet} \rightarrow CH_3^{\bullet} + H_2O$ (transfer protonu)

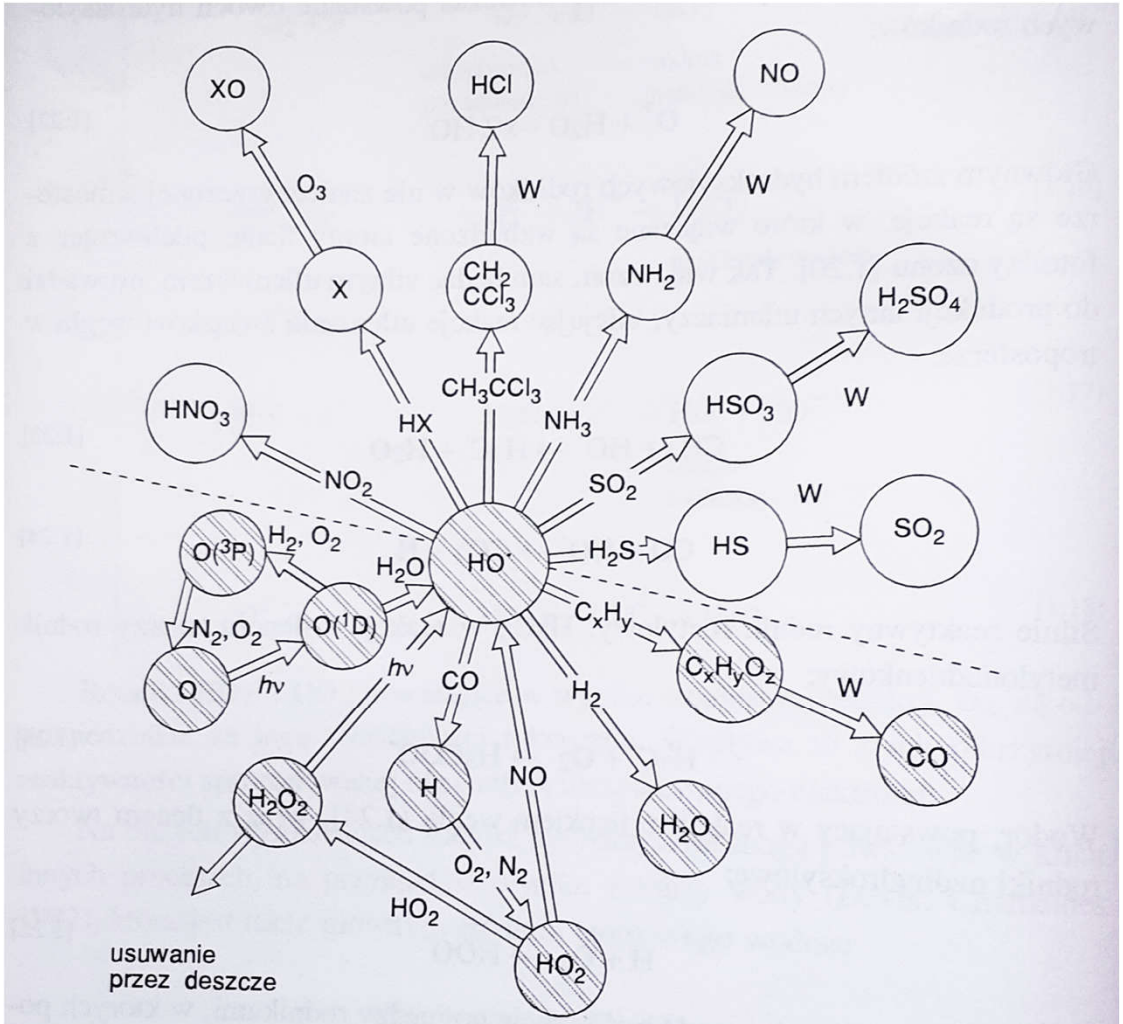
$CH_3^{\bullet} + O_2 \rightarrow CH_3OO^{\bullet}$ (silnie reaktywny rodnik metylo-nadtlenkowy)

$CO + OH^{\bullet} \rightarrow CO_2 + H$ (utlenianie CO, produkcja H)

$H + O_2 \rightarrow HOO^{\bullet}$ (rodnik nad-hydroksylowy) itd. itp.

L. Falkowska, K. Korzeniewski, *Chemia atmosfery*, Wyd. UG 1998, str. 33

Rodnik hydroksylowy – detergent (oczyszczacz) atmosfery



Rys. 1.8. Reakcje z udziałem rodników hydroksylowych, kontrolujące poziom stężeń gazowych związków siarki węgla i azotu w troposferze (Monahan 1983). Procesy zachodzące poniżej linii przerywanej należą do najbardziej zaangażowanych w usuwanie rodników hydroksylowych HO· w troposferze. Procesy powyżej linii kontrolują stężenia HO· przez wiązanie związków azotu, węgla i siarki w wieloetapowych reakcjach (W). Zasoby związku w atmosferze symbolizuje wielkość okręgu, halogenki oznaczone są jako C_xH_y, $O(^3P)$ oznacza atom tlenu w stanie podstawowym, $O(^1D)$ – atom tlenu w stanie wzbudzonym, a strzałki – kierunek reakcji

34

$CH_4 + OH^{\bullet} \rightarrow CH_3^{\bullet} + H_2O$
(produkcja wody w stratosferze)

$NO_2 + OH^{\bullet} \rightarrow HNO_3^{\bullet}$
(„wymywanie: NO_2)

I cały łańcuch reakcji:

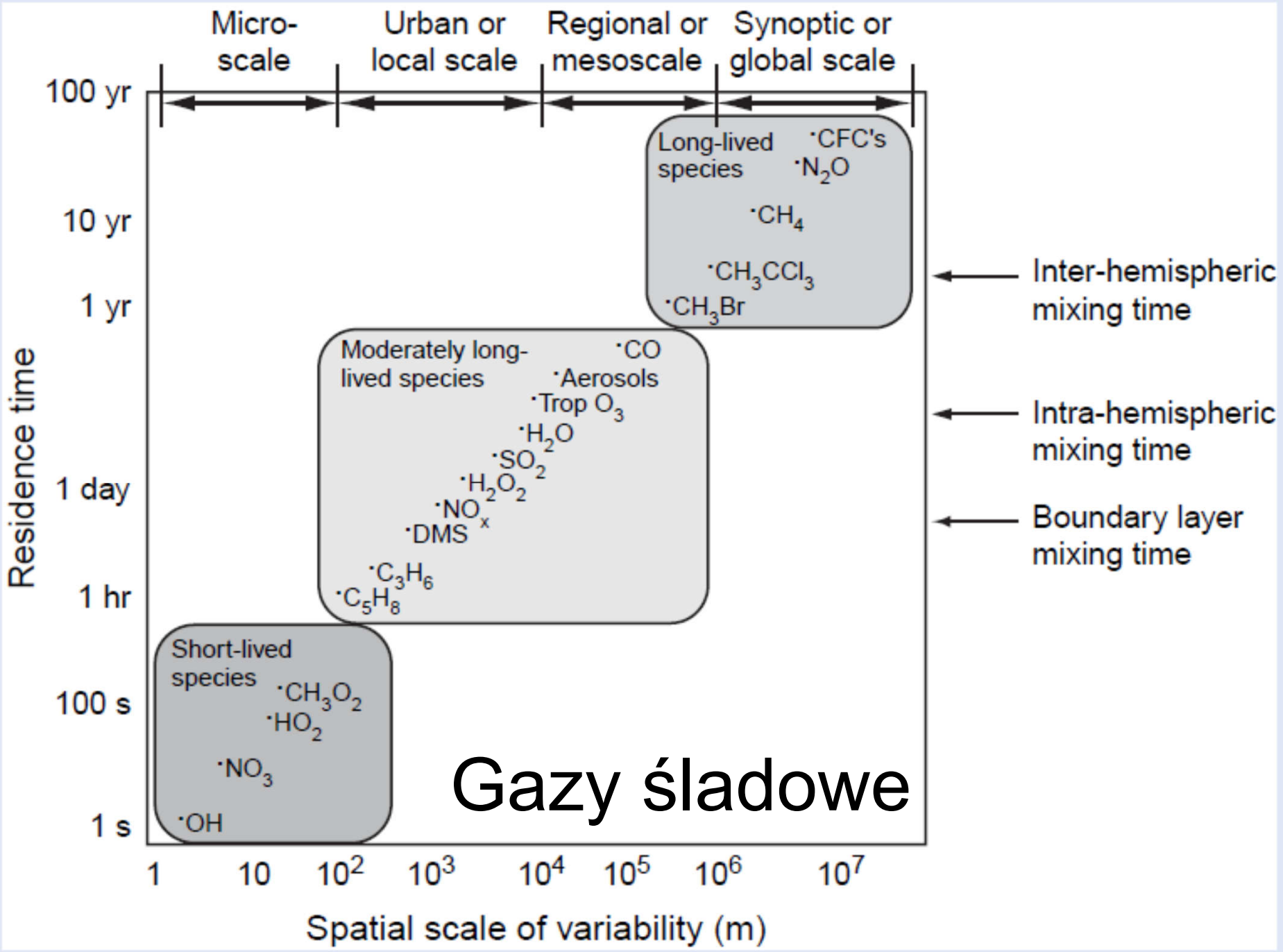
$CO + OH^{\bullet} + O_2 \rightarrow CO_2 + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$
(utlenianie NO)

$NO_2 + h\nu \rightarrow NO + O$ (dysocjacja dwutlenku azotu, produkcja O)

$O + O_2 + M \rightarrow O_3 + M$
(produkcja ozonu)

(*Atmospheric Science*, srt. 167)



Spatial and temporal scales of variability for some atmospheric constituents. The temporal scale

International Atomic Energy Agency

Atomic Molecular Data Services

Provided by the Nuclear Data Section

G. Karwasz. IAEA Meeting, Vienna, 23.11.2019

„Recommended" cross sections for electron scattering with molecules

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Hyuck Cho
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Rationale: edge and divertor plasma

Influence of atomic physics on EDGE2D-EIRENE simulations of JET divertor detachment with carbon and beryllium/tungsten plasma-facing components

Table 3. Atomic and molecular reactions included in the physics models used in EIRENE (also valid for D).

NIMBUS-like model	Kotov-2008 model
(1) $e + H^0 \rightarrow 2e + H^+$	Same reactions as default plus:
(2) $H^+ + H^0 \rightarrow H^0 + H^+$	(9) $H_2 + H^+ \rightarrow H^+ + H_2$
(3) $e + C^0 \rightarrow 2e + C^+$	(10) $H_2 + H^+ \rightarrow H_2^+ + H^0$
(4) $e + H_2 \rightarrow 3e + 2H^+$	(11) $e + H_2 \rightarrow 2e + H_2^+$
(5) $e + H_2 \rightarrow e + 2H^0$	(replacing (4))
(6) $e + H_2 \rightarrow 2e + H^+ + H^0$	(12) $e + H_2^+ \rightarrow e + H^0 + H^+$
(7) $e + H^+ \rightarrow H^0$	(13) $e + H_2^+ \rightarrow 2e + 2H^+$
(8) $2e + H^+ \rightarrow e + H^0$	(14) $e + H_2^+ \rightarrow 2H^0$
No CRM[a] for (4), (5) and (6)	CRM[a] for (11), (5) and (6)

[a] Collisional Radiative Model.

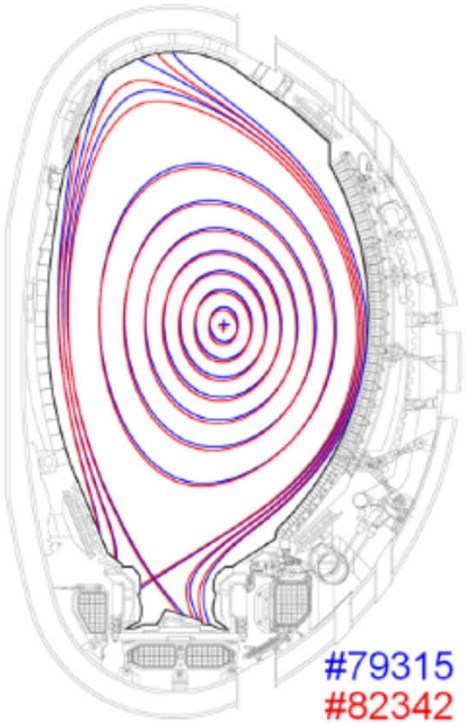


Figure 1. Magnetic equilibria for the shots #79315 and #82342 at 20 s and 13 s, respectively.

Guillemaut et al. Nucl.Fusion **54** (2014) 093012

Data needed:

I Neutrals (H, C, C_2, Be, BeH_2, CH_4)

1. Total cross section

2. Partial cross sections:

elastic scattering e+A →e+A (from 0 eV)

rotational excitation $e+CH_4\ (J=0) \rightarrow e+CH_4\ (J=2)$ i.e. 5 meV

vibrational excitation $e+AB(v=0) \rightarrow e+AB(v>0)$ i.e. 50 meV

electron attachment (dissociative) $e+AB \rightarrow A^- + B$ 5 eV

electronic excitation $e+A \rightarrow e+A^*$ 5 eV

emission lines: $A^* \rightarrow A + h\nu$

neutral dissociation $e+AB \rightarrow A + B + e$ 5 eV

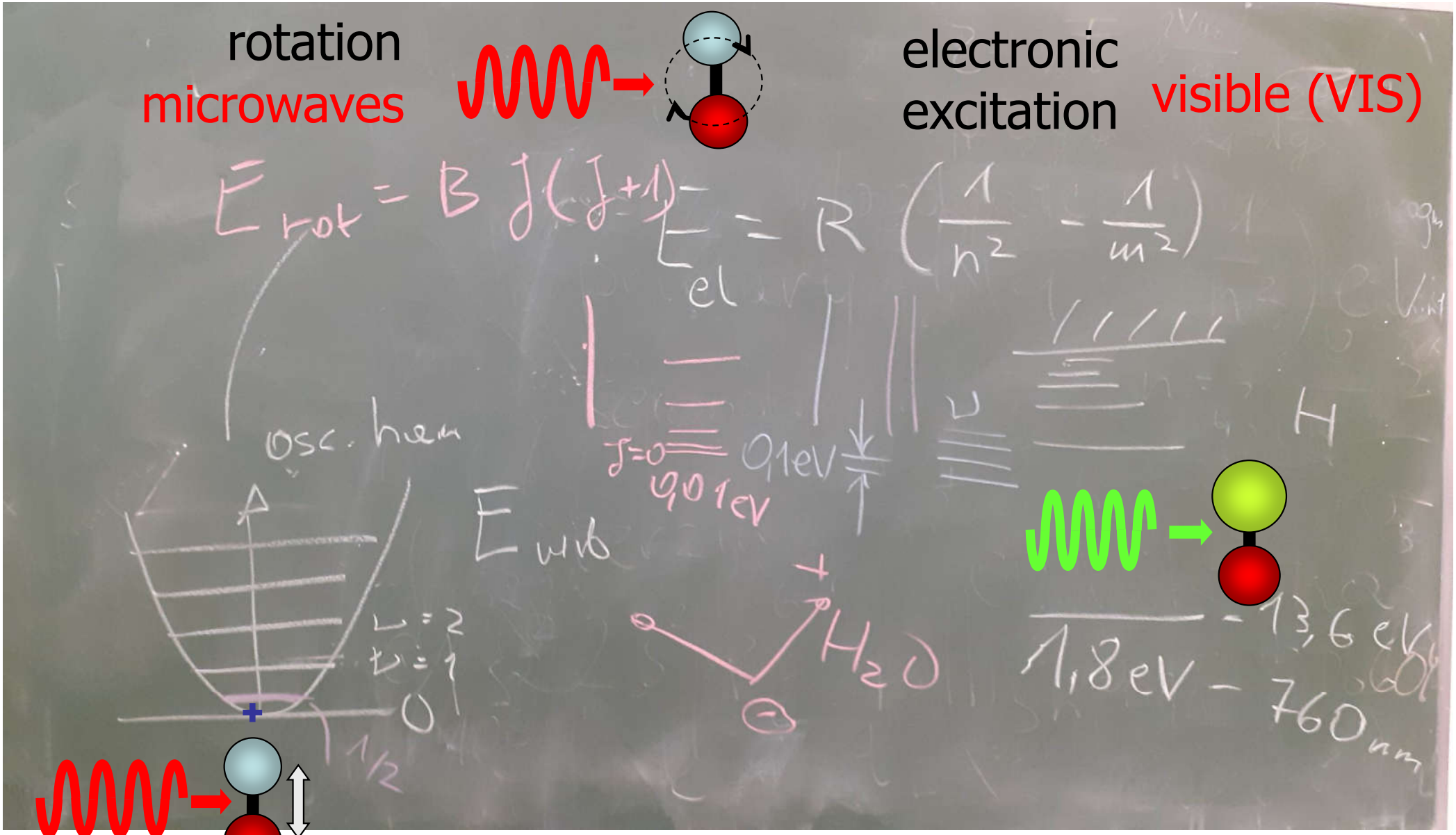
emisison from dissociation $e + AB \rightarrow A^* + B + e + h\nu$

ionization $e+A \rightarrow A^+ + 2e$ 10 eV

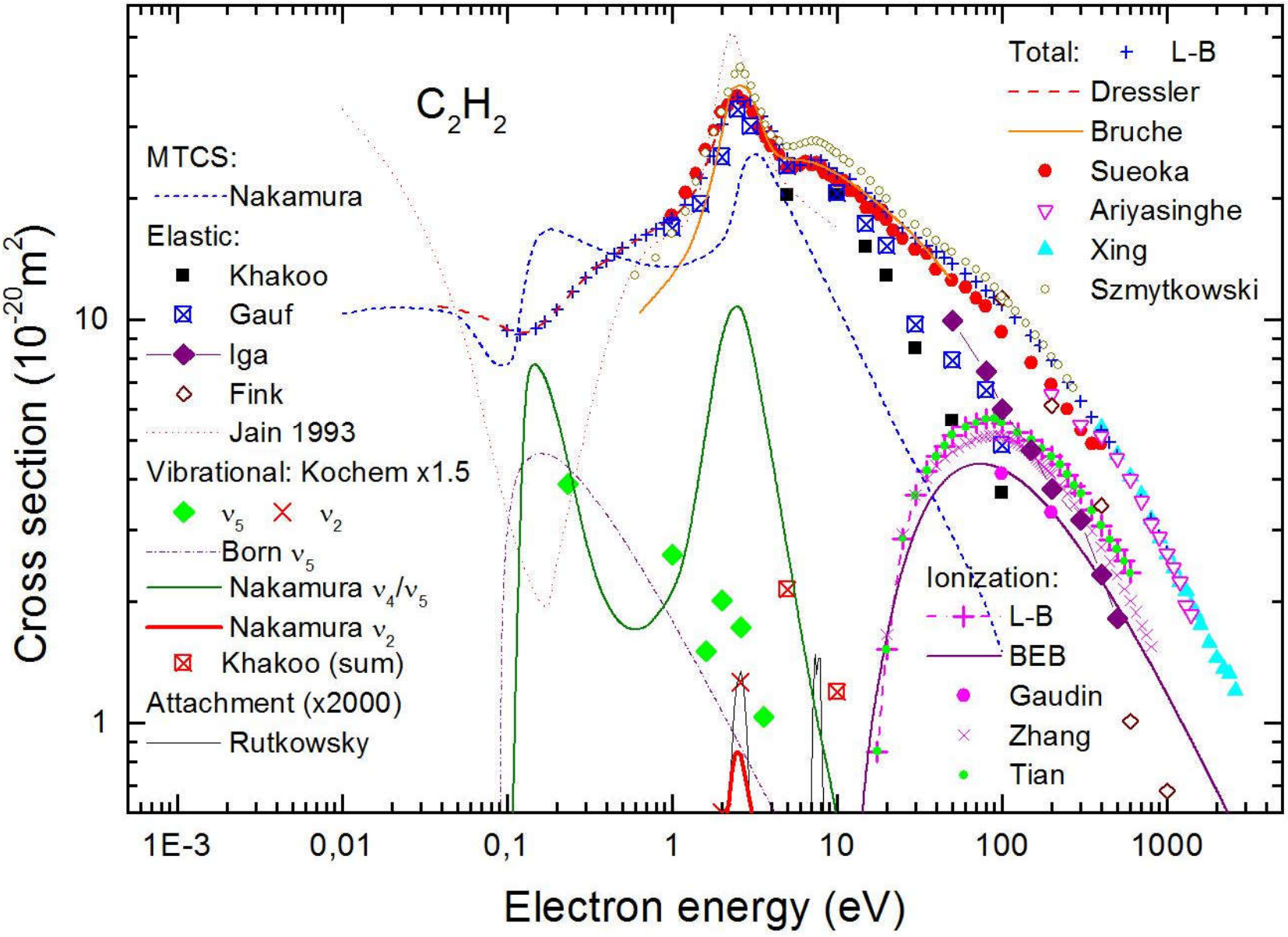
dissociative ionization $e+AB \rightarrow A + B^+ + 2e$ 25 eV

ionization into excited states $e + A \rightarrow (A^+)^* + 2e$ 15 eV

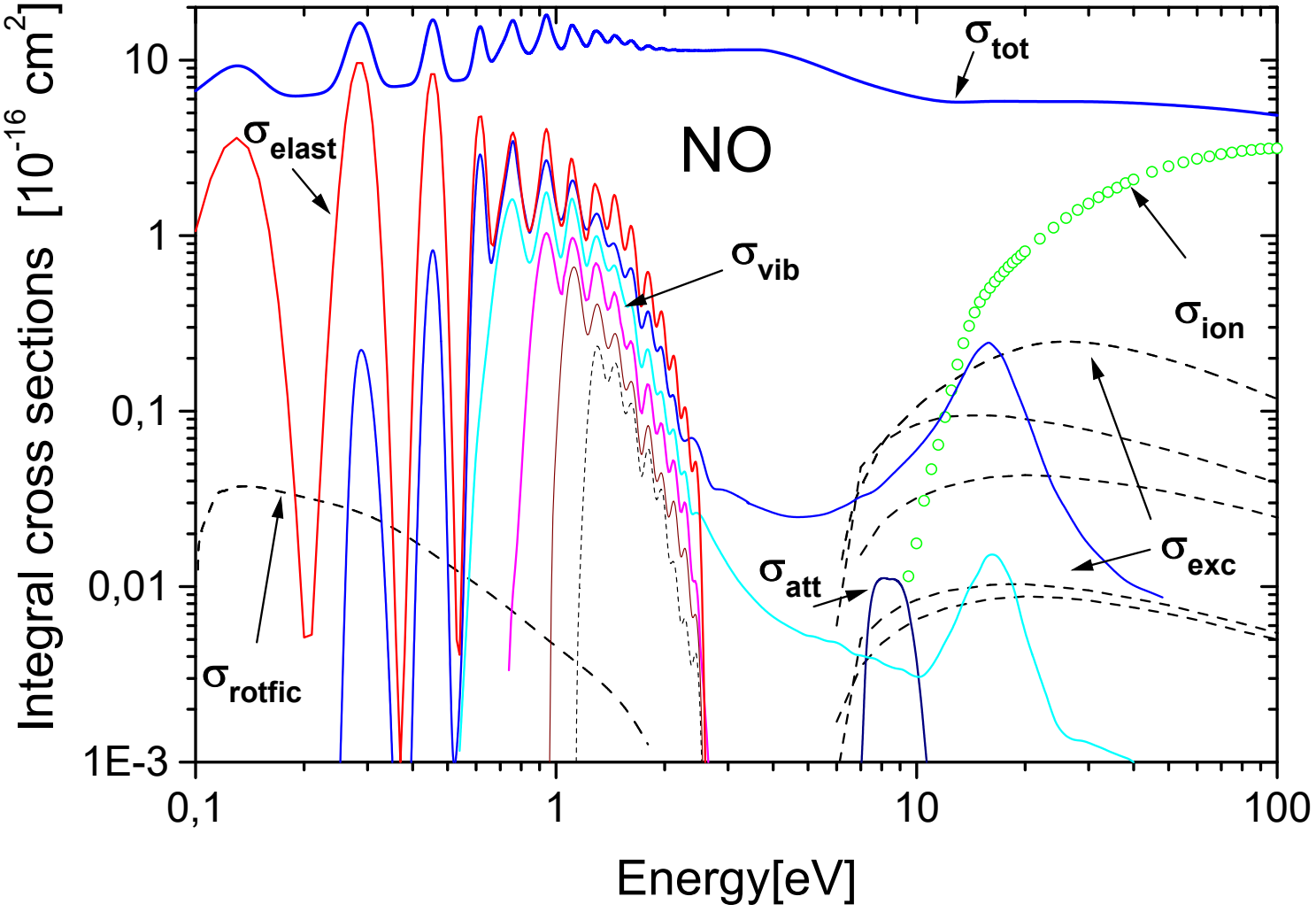
Energy levels



Total & partial cross sections: C_2H_2

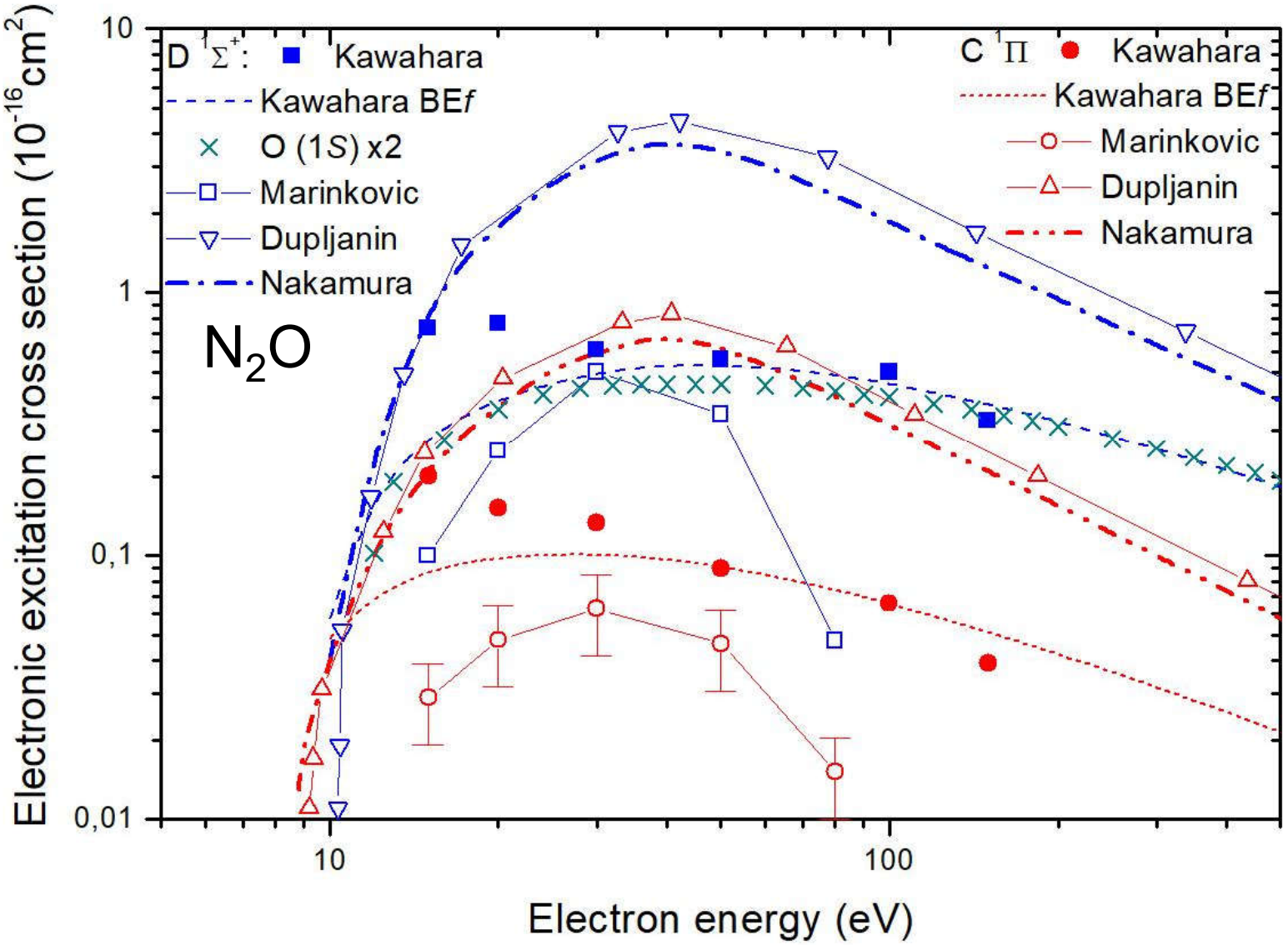


NO – high (resonant) vibrational cross section at low energies: polar glow



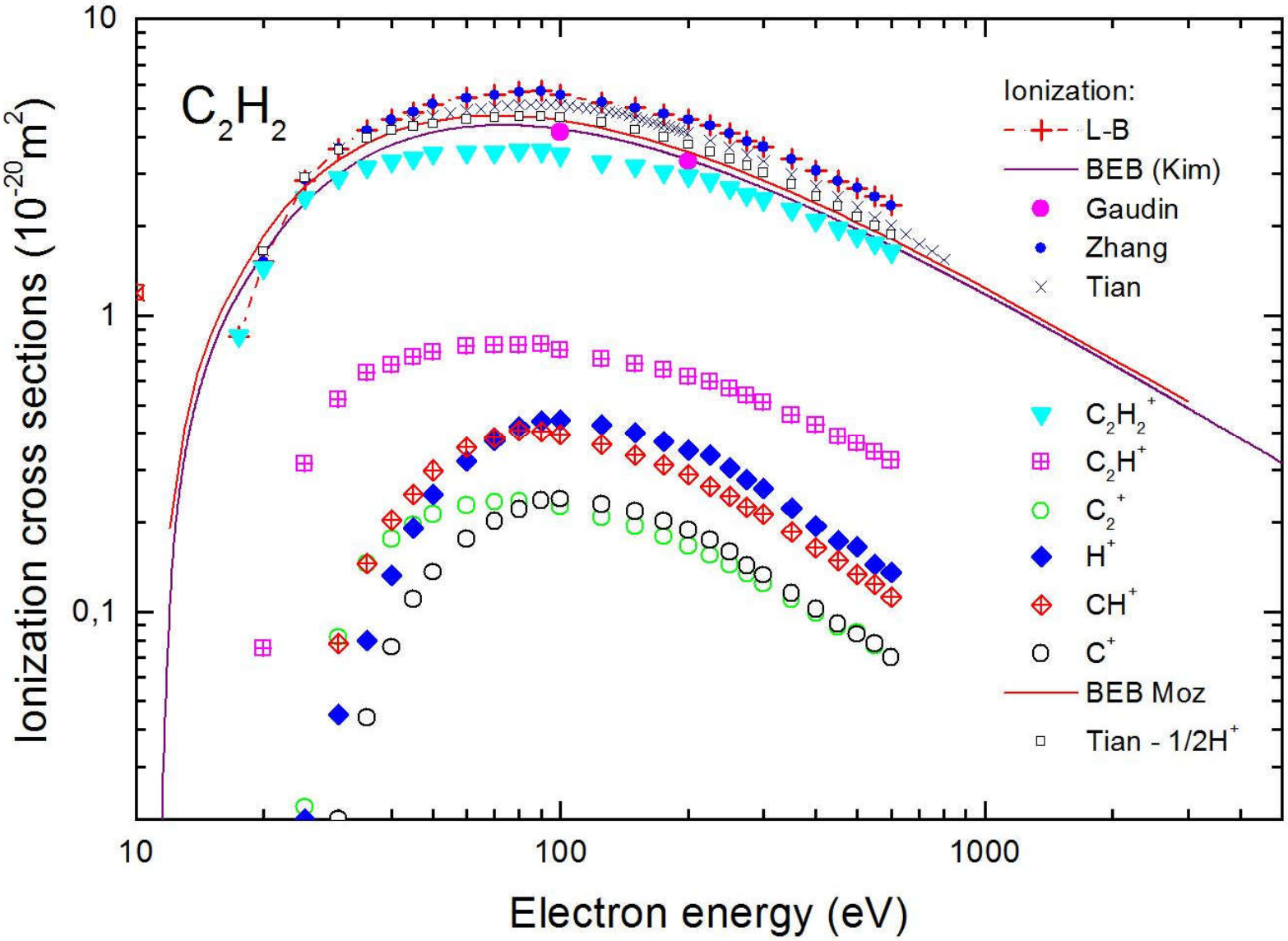
NO + e⁻ → NO⁻ (electron attachment)

Electronic excitation: optically allowed and forbidden states



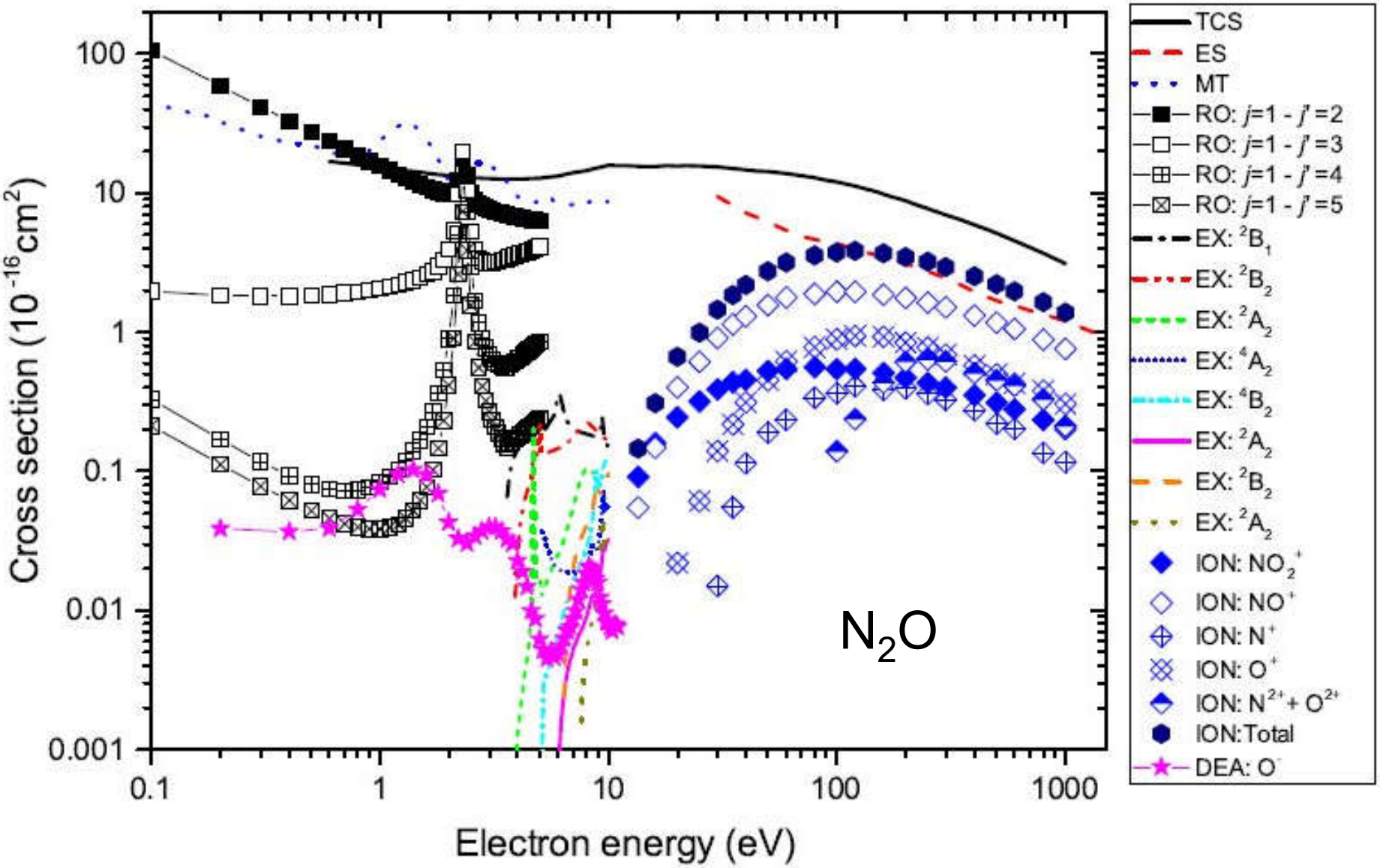
Electronic excitation is relatively small part of total (or ionization) cross section

Ionization: partial



Electron-impact ionization produces a whole „zoo” of ionic fragments

„Recommended” cross-sections



Cross Sections for Electron Collisions with Molecular and Atomic Oxygen

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(Revised 23 January 2025)

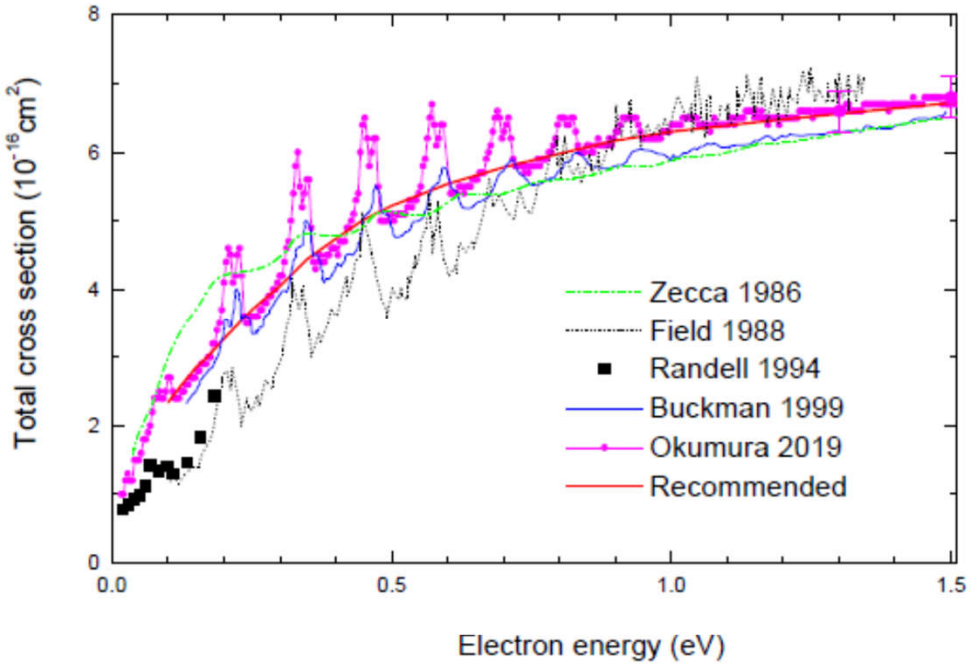

FIG. 2. Experimental total cross sections for electron scattering from O_2 in the very-low energy range: green dash-dot line,

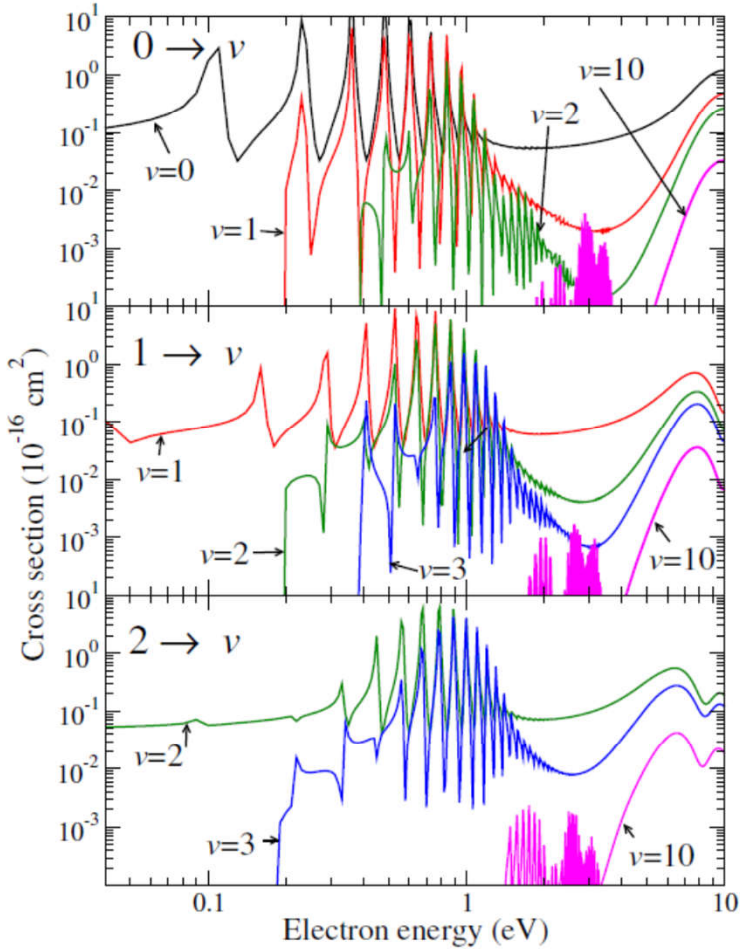

FIG. 7. Examples of the recommended cross sections for vibrational excitation for several transition obtained by La-

Very-low energy resonant scattering

Electronic excitations and transitions between states

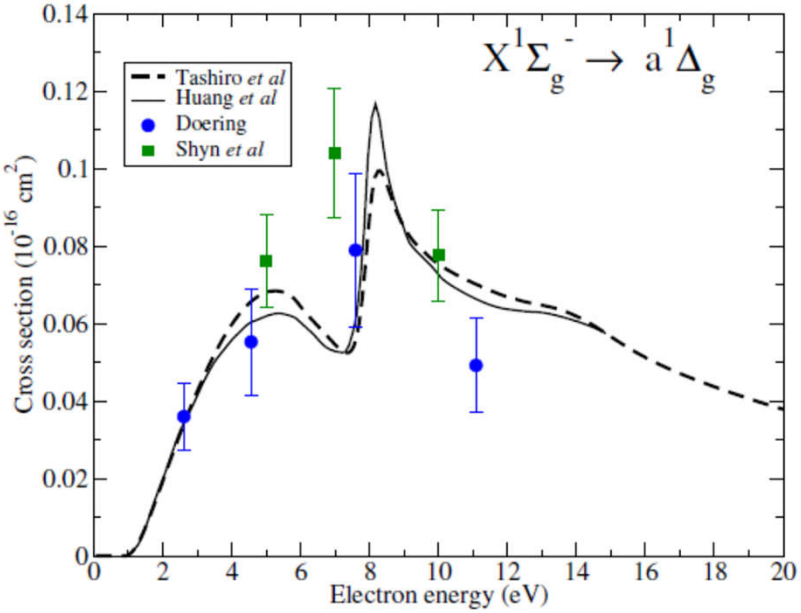

FIG. 8. Electronic excitation cross section for the $X\ ^3\Sigma_g^- \rightarrow a\ ^1\Delta_g$ transition. The solid line - Huang, Zhang,

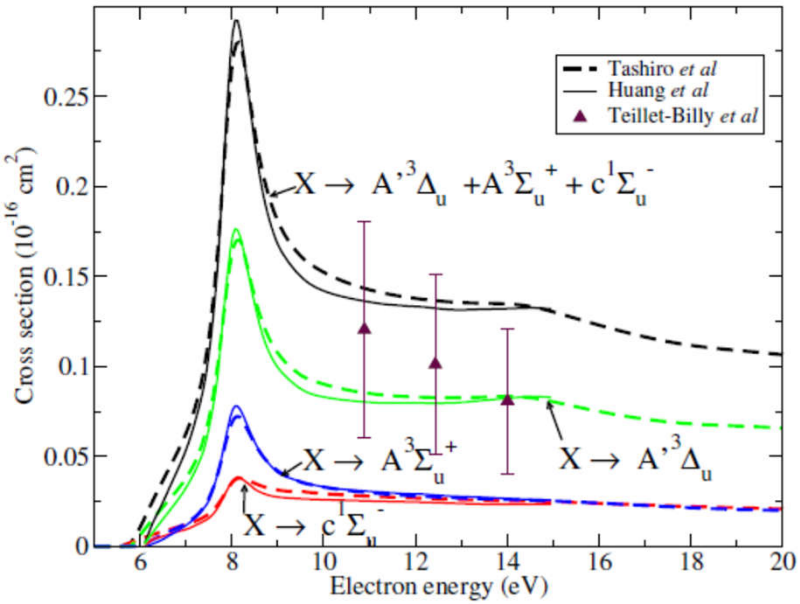

FIG. 10. Electronic excitation cross section for the $X\ ^3\Sigma_g^- \rightarrow c^1\Sigma_u^-$ (red lines), $X\ ^3\Sigma_g^- \rightarrow A^3\Sigma_u^+$ (blue lines), and

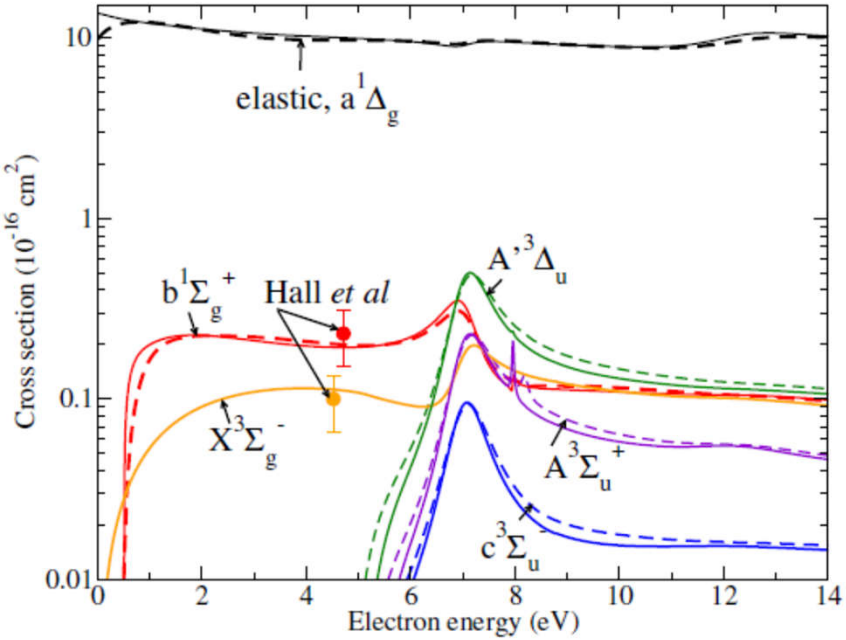

FIG. 11. Cross sections for elastic and inelastic transi-

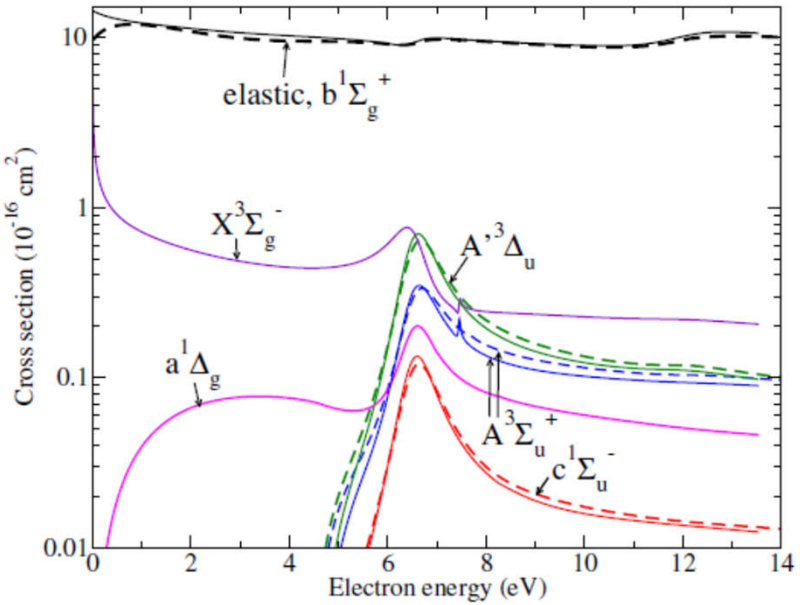

FIG. 12. Similar to Fig. 11 for the elastic and inelastic transitions starting from the metastable $b\ ^1\Sigma_g^+$ state. The cross sections are taken from Ref.[71].

THE ASTROPHYSICAL JOURNAL SUPPLEMENT SERIES, 204:20 (45pp), 2013 February doi:10.1088/0067-0049/204/2/20(

Titan's atmosphere

CRITICAL REVIEW OF N, N^+, N_2^+, N^{++}, And N_2^{++} MAIN PRODUCTION PROCESSES AND REACTIONS OF RELEVANCE TO TITAN'S ATMOSPHERE

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ABSTRACT

This paper is a detailed critical review of the production processes and reactions of N, N^+, N_2^+, N^{++}, and N_2^{++} of relevance to Titan's atmosphere. The review includes neutral, ion–molecule, and recombination reactions. The review covers all possible active nitrogen species under Titan's atmospheric conditions, specifically N_2 ($A\ ^3\Sigma_u^+$), N (^4S), N (^2D), N (^2P), N_2^+, N^+ (^3P), N^+ (^1D), N_2^{++}, and N^{++} species, and includes a critical survey of the reactions of N, N^+, N_2^+, N^{++}, and N_2^{++} with N_2, H_2, D_2, CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8 and the deuterated hydrocarbon analogs, as well as the recombination reactions of N_2^+, N^+, N_2^{++}, and N^{++}. Production processes, lifetimes, and quenching by

Dissociation and Ionization Thresholds of N_2, as well as Lifetimes of Excited States

	Species	Threshold Energy (eV)	Remarks
	$N_2\ (X\ ^1\Sigma_g^+)$	0	
1)	$N_2\ (A\ ^3\Sigma_u^+)$	6.22	N_2 (A) lifetime = 2.37 s (a)
	N (^4S) + N (^4S)	9.76	Not observed
2)	N (^2D) + N (^4S)	12.14	N (^2D) lifetime = 13.6 hr and 36.7 hr * (b)
	N (^2P) + N (^4S)	13.33	N (^2P) lifetime = 11.1 s and 10.5 s ** (b)
	N (^2D) + N (^2D)	14.52	
3)	$N_2^+\ (X\ ^2\Sigma_g^+)$	15.58	
	$N_2^+\ (A\ ^2\Pi_u)$	16.93	N_2^+ (A) lifetime = 13.9 – 7.3 ms *** (c)
	$N_2^+\ (B\ ^2\Sigma_u^+)$	18.75	N_2^+ (B) lifetime = 67 ns (d)
4)	N^+ (^3P) + N (^4S)	24.29	
	N^+ (^1D) + N (^4S)	26.19	N^+ (^1D) lifetime = 258 s (e)
	N^+ (^3P) + N (^2D)	26.68	
	N^+ (^3P) + N (^2P)	27.87	Not observed
	N^+ (^1S) + N (^4S)	28.35	Not observed
	$N_2^{++}\ (X\ ^1\Sigma_g^+)$	42.88	N_2^{++} lifetime = 3 s (f)
	N^+ (^3P) + N^+ (^3P)	44.5	
	N^{++} (^2P) + N (^4S)	53.9	Appearance energy is 55.2 eV (g)

1) Lowest electronic excited state – very long lived
2) Threshold for dissociation into neutral fragments (metastable); 12.1 eV – nitrogen N_2 is one of the most stable molecules
3) Ionization threshold 15.6 eV (much higher than H atom)

Many reactants, many channels, many but non congruent data

Table 3
Rate Constant Measurements for the Neutral N_2 ($A\ ^3\Sigma_u^+$) and N (^2D, ^2P) Reactions

Reaction	T (K)	k ($cm^3\ s^{-1}$)	Method	Reference
N_2 ($A\ ^3\Sigma_u^+$) + N_2	298	$\leqslant 10 \times 10^{-18}$	FP-CL	(Callear & Wood 1971)
N_2 ($A\ ^3\Sigma_u^+$) + N_2	298	$\leqslant 3.7 \times 10^{-16}$	PR-RA	(Dreyer & Perner 1973)
N_2 ($A\ ^3\Sigma_u^+$) + N_2	298	4.5×10^{-17}	DF	(Vidaud et al. 1976)

Reaction	T (K)	k ($cm^3\ s^{-1}$)	Method	Reference
N_2 ($A\ ^3\Sigma_u^+$) + C_3H_8	298	1.3×10^{-12}	FP-ES	(Callear & Wood 1971)
N_2 ($A\ ^3\Sigma_u^+$) + C_3H_8	298	1.3×10^{-12}	Compilation	(Herron 1999)
N (^2D) + N_2	298	$\leqslant 6 \times 10^{-15}$	FP-CL	(Black et al. 1969)
N (^2D) + N_2	298	1.6×10^{-14}	DF-RA	(Lin & Kaufman 1971)

Products:

Recommended yields: (H_2CN + H)/(HCN + H + H), 0.90/0.10.

The N (^4S) + CH_3 reaction has three exothermic channels:

N (^4S) + CH_3 → H_2CN + H −1.59 eV

→ HCN + H + H −0.50 eV

→ HCN + H_2 −5.02 eV.

Thunderstorm: electric discharge 1,3 GV

https://physics.aps.org/articles/v12/29?utm_campaign=weekly&utm_medium=email&utm_source=emailalert

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Focus: Muons Reveal Record-Breaking Thunderstorm Voltage

March 15, 2019 • *Physics* 12, 29

March 15, 2019• *Physics* 12, 29

A thunderstorm probed with atmospheric muons had an electric potential exceeding one billion volts, much higher than values measured previously.

Print

Measurement of the Electrical Properties of a Thundercloud Through Muon Imaging by the GRAPES-3 Experiment

B. Hariharan, A. Chandra, S. R. Dugad, S. K. Gupta, P. Jagadeesan, A. Jain, P. K. Mohanty, S. D. Morris, P. K. Nayak, P. S. Rakshe, K. Ramesh, B. S. Rao, L. V. Reddy, M. Zuberi, Y. Hayashi, S. Kawakami, S. Ahmad, H. Kojima, A. Oshima, S. Shibata, Y. Muraki, and K. Tanaka (GRAPES-3 Collaboration)

Phys. Rev. Lett. 122, 105101 (2019)

Published March 15, 2019

Features

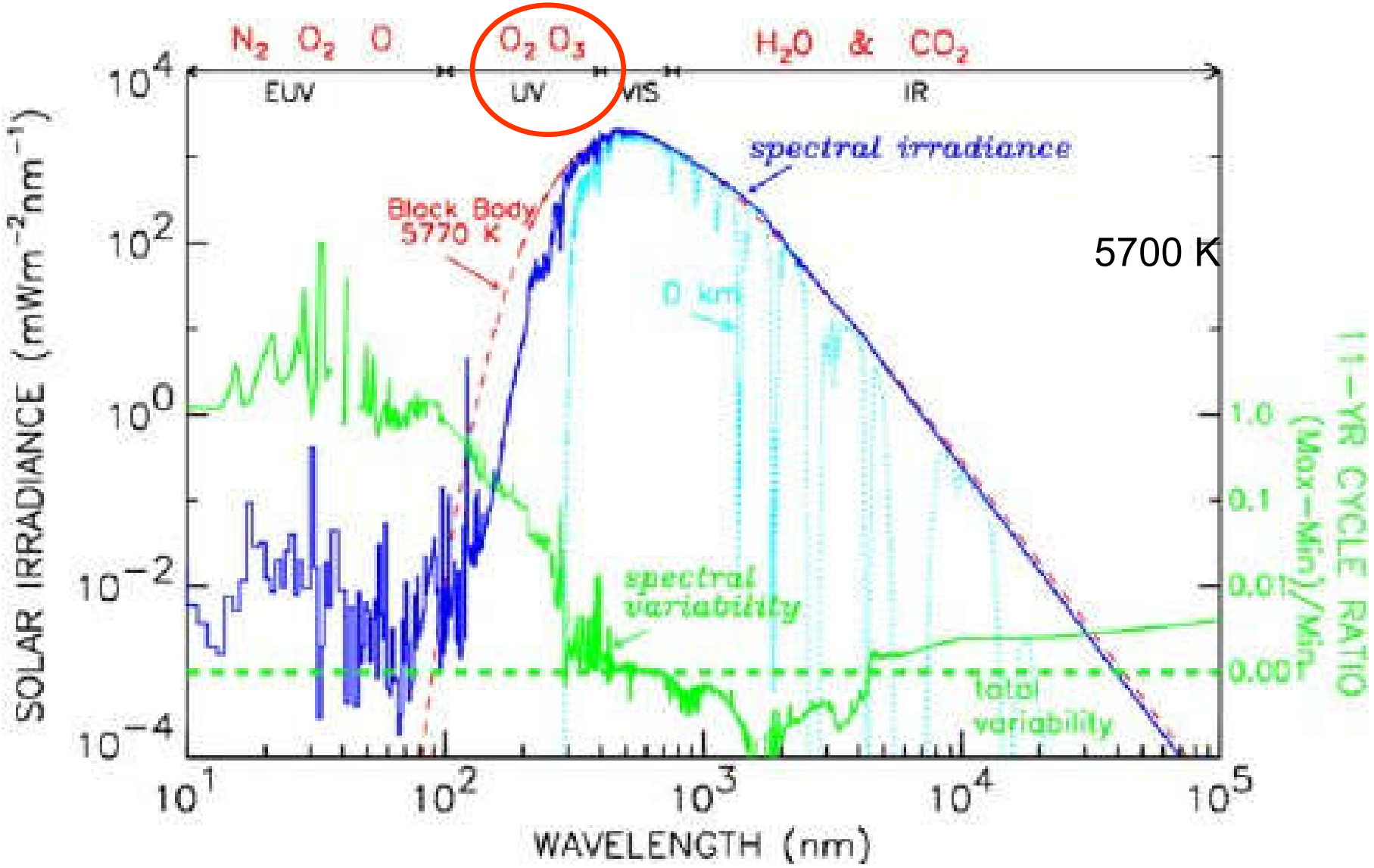
How to Get Raves for Your *Reviews*

At a celebration for the 90th anniversary of

Researchers have documented a thunderstorm producing an electric potential of about **1.3 billion volts (GV),** 10 times greater than the largest value ever reported.

Van der Graaf, spawarka, łuk plamozwy

Widmo Słońca, poza atmosferą

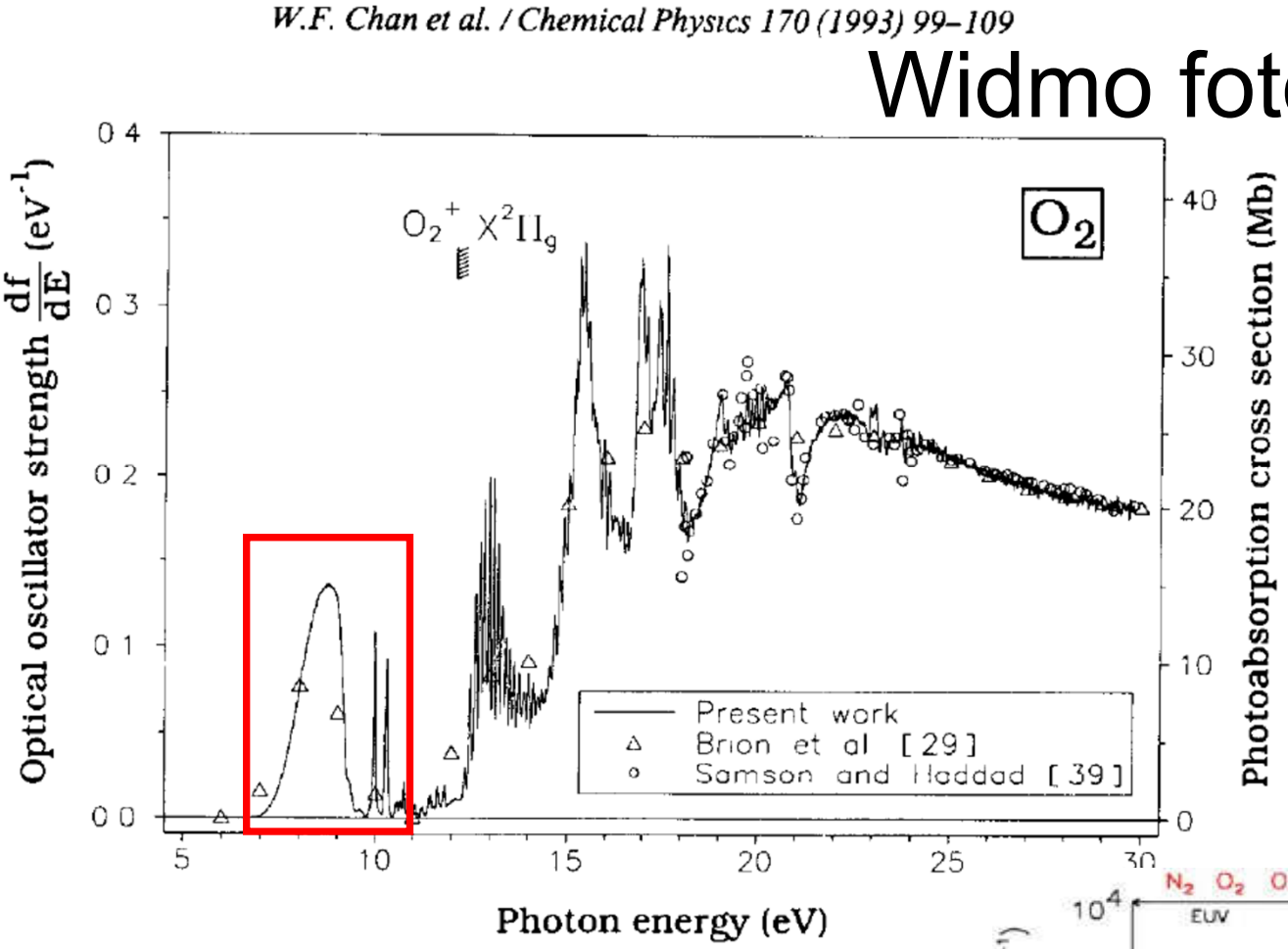


Wiosną jest znacznie więcej UV niż jesienią: latem powstaje ozon

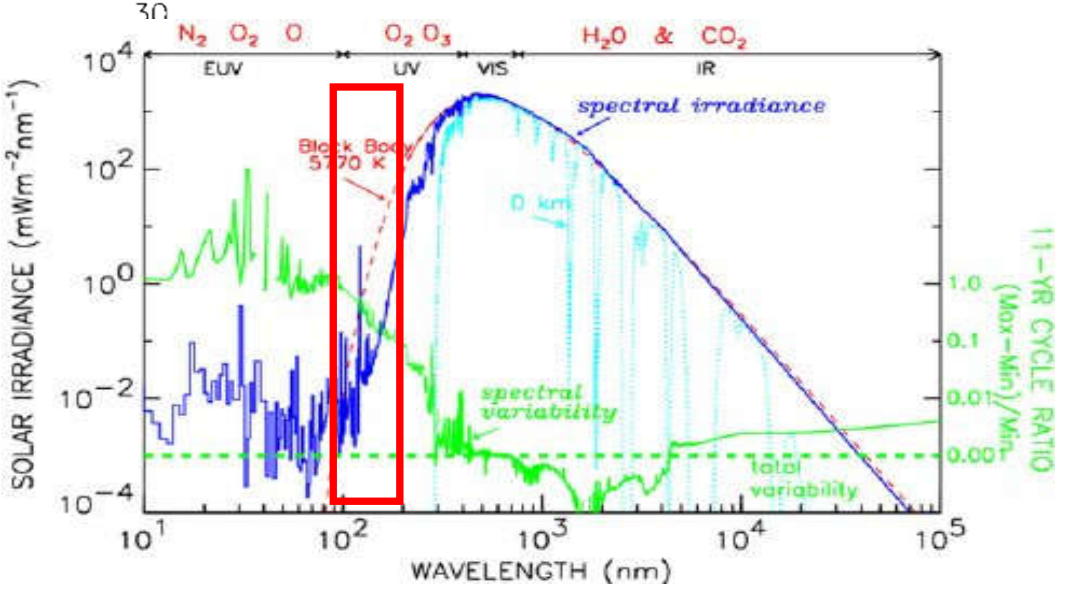
Asta Juzeniene et al. , Solar radiation and human health

•Reports on Progress in Physics 74(6):066701.May 2011, DOI: 10.1088/0034-4885/74/6/066701

Widmo fotoabsorpcji O_2

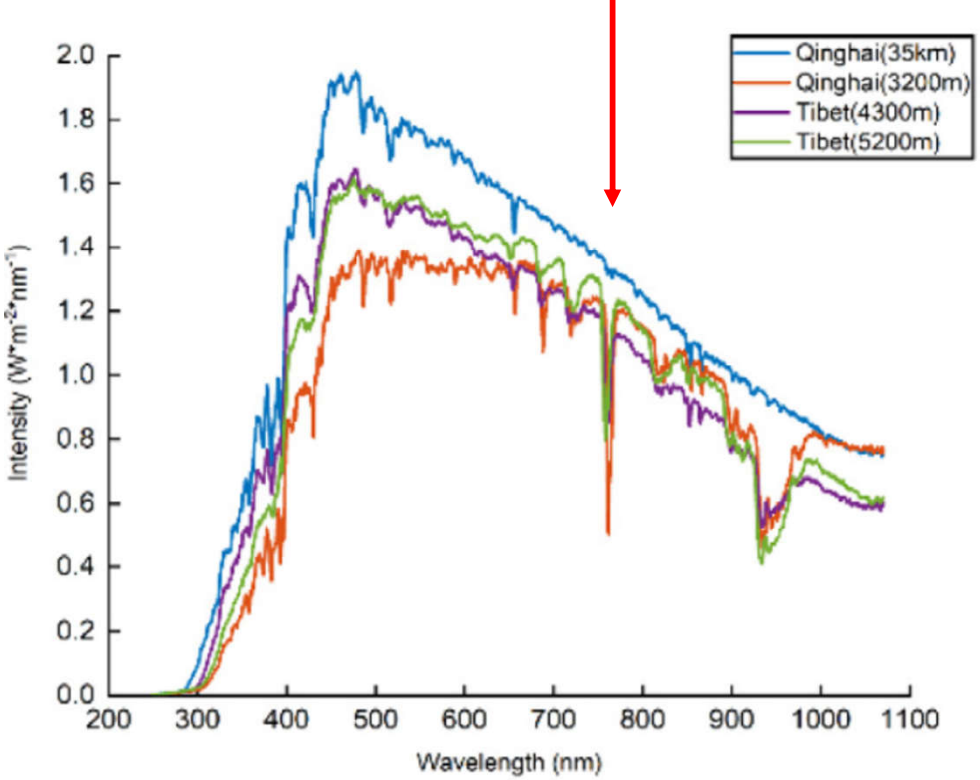


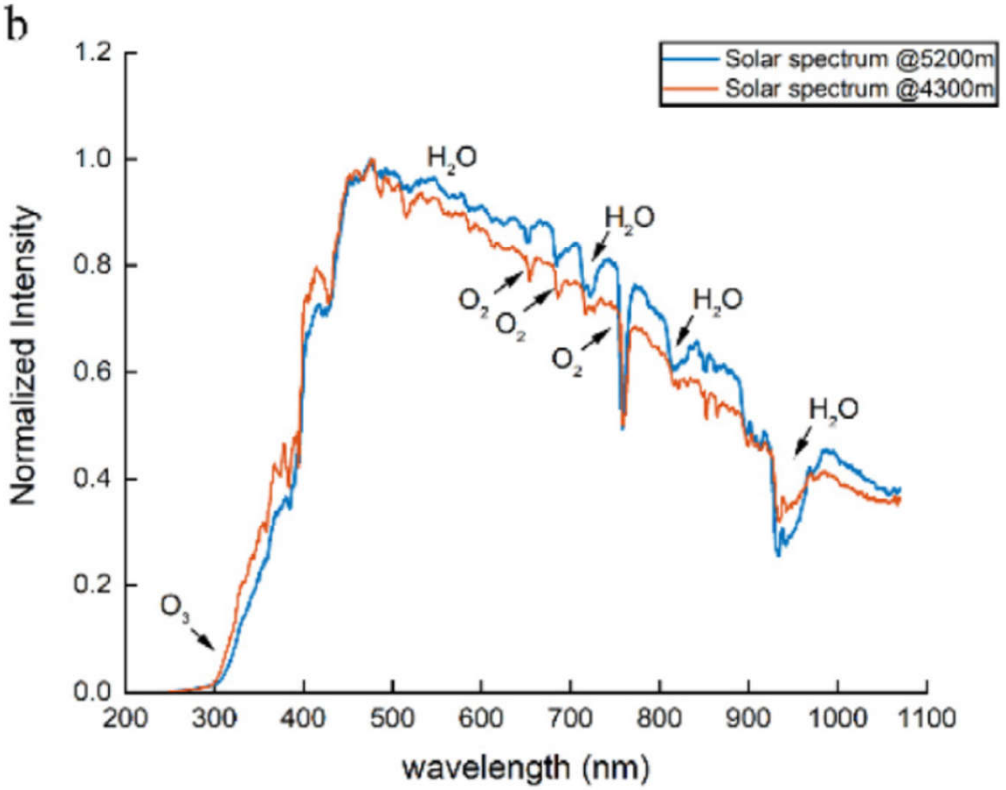
6.5 - 12 eV
tj. c.a. 100 – 200 nm



Absorpcja optyczna tlenu (O_2)

O_2 b $^1\Sigma_g$ metastable state

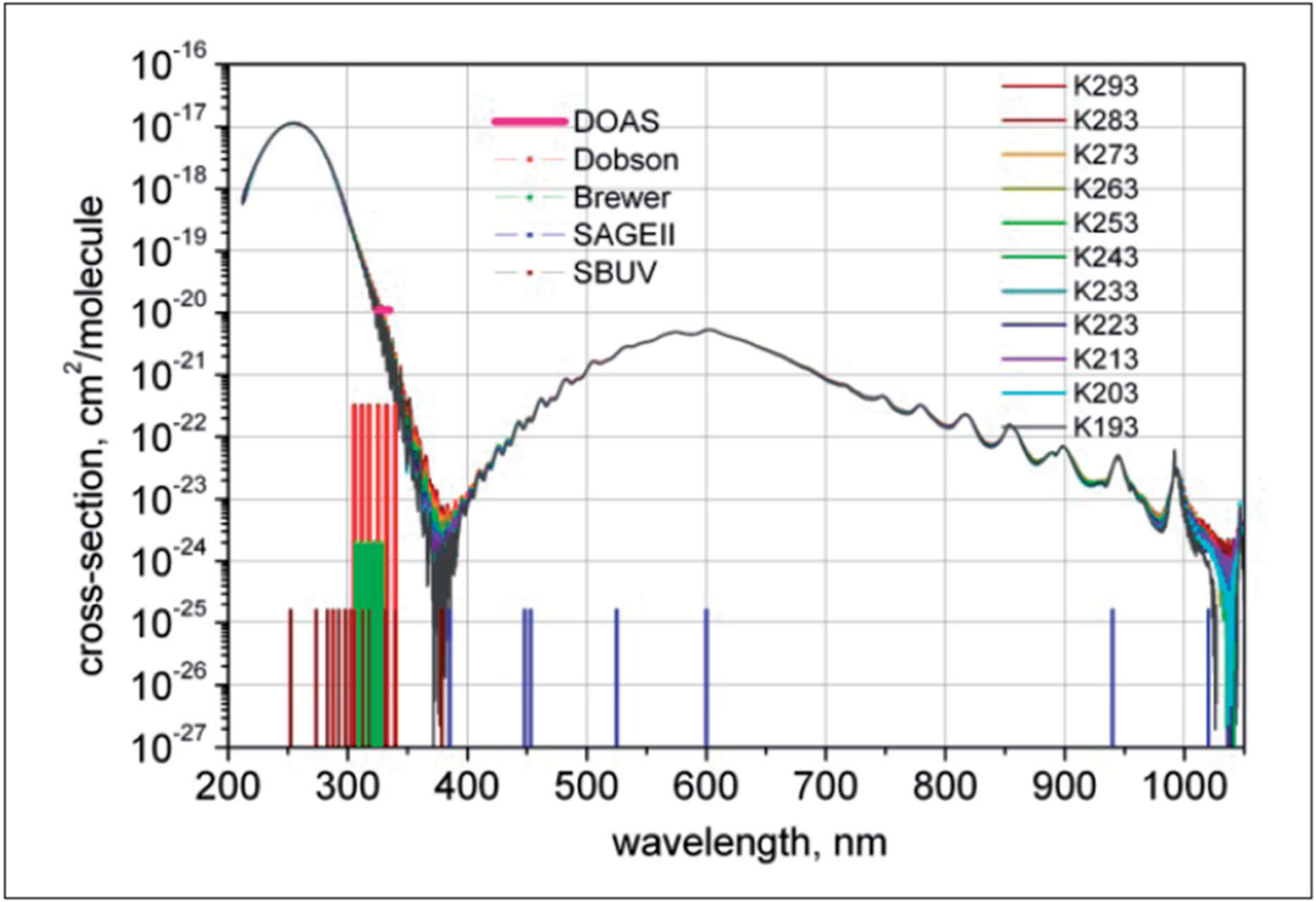




Tlen cząsteczkowy – tylko w troposferze,
na wysokości 35 km – brak absorpcji linii 760 nm

Xu i in., 2023, https://doi.org/10.1016/j.egyr.2023.04.229
Pomiary za pomocą balonu stratosferycznego

Widmo absorpcji UV, VIS i IR ozonu O_3



https://www.spectroscopyeurope.com/article/new-broadband-high-resolution-ozone-absorption-cross-sections

Rodnik („detergent”) OH^-

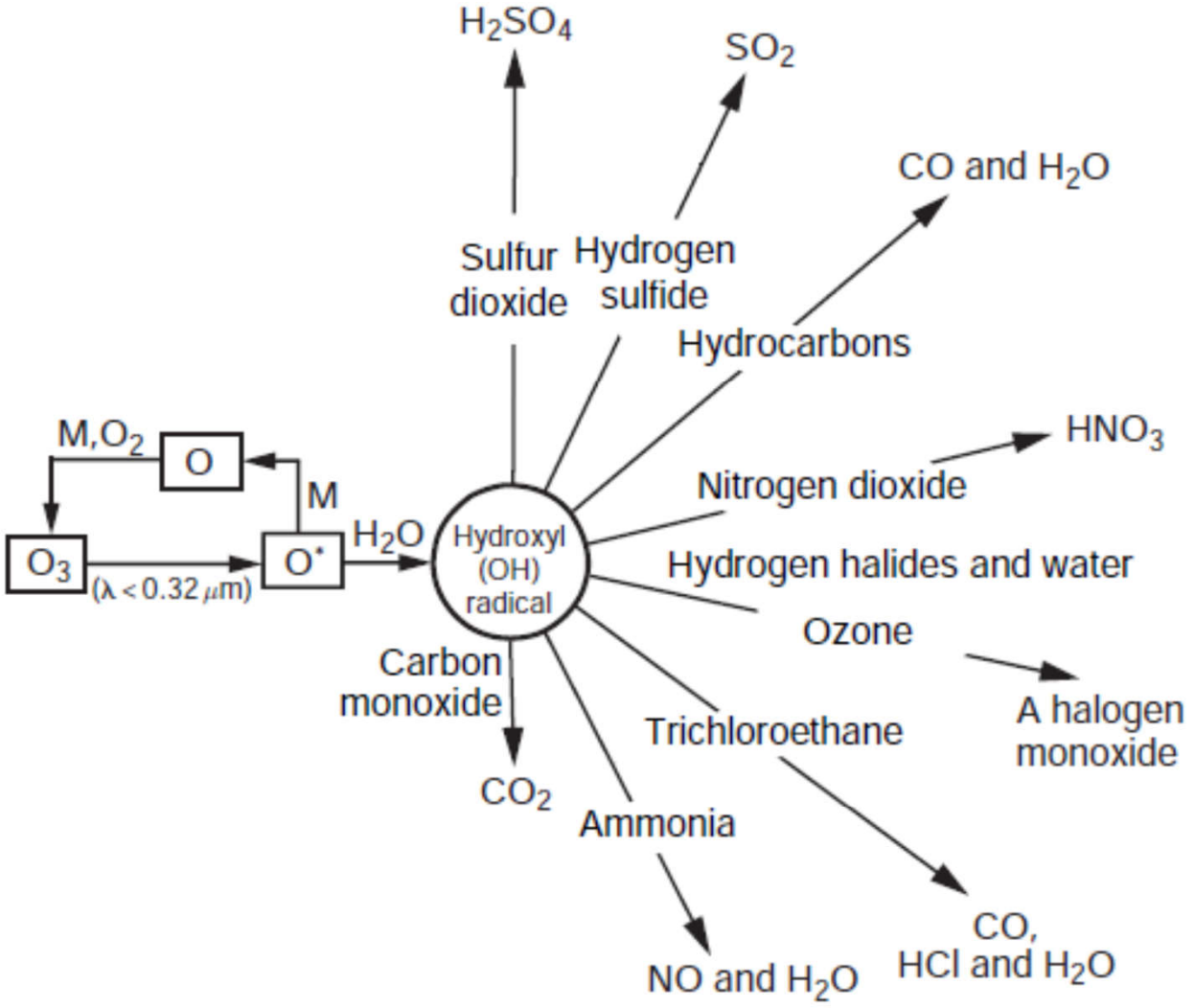


Fig. 5.4 Illustration of the central role of the OH radical in the oxidation of tropospheric trace gases. Little escapes oxidation by OH. [Adapted from *Global Tropospheric Chemistry*,

Atmospheric Science, str. 163

Bilans azotu

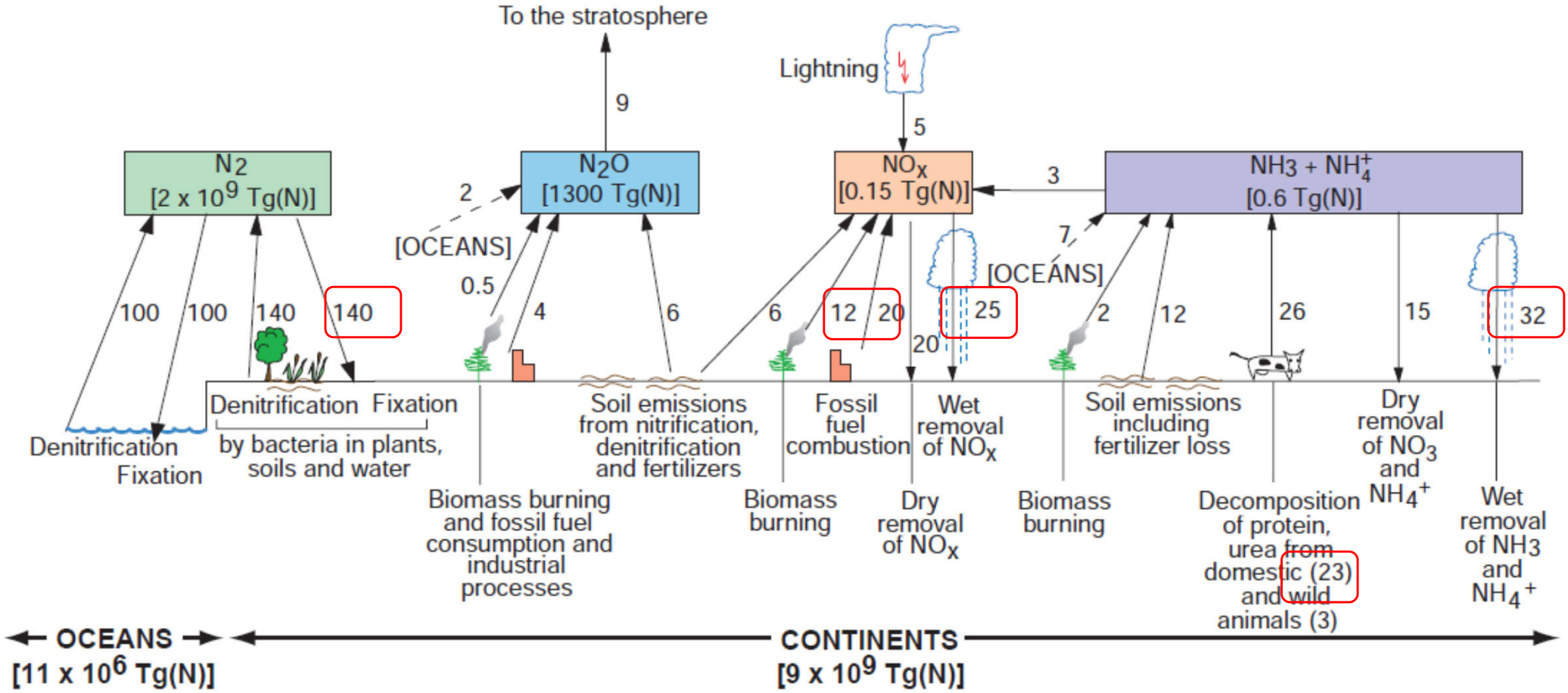


Fig. 5.14 Principal sources and sinks of nitrogen-containing gases in the atmosphere. Numbers alongside the arrows are estimates of average annual fluxes in Tg(N) per year; various degrees of uncertainty, some quite large, are associated with all of the fluxes. Numbers in square brackets are total amounts of the species in the atmosphere. [Adapted from P. V. Hobbs, *Introduction to Atmospheric Chemistry*, Camb. Univ. Press, 2000, p. 148. Reprinted with the permission of Cambridge University Press.]

[1300] – całkowita zawartość w atmosferze; 4 – roczny przepływ (w Tg azotu)
140 – absorpcja N przez bakterie azotowe; 25+32 – wymywanie NO_x w deszczu
23 – mocz i dekompozycja białek zwierząt hodowlanych

Bilans siarki

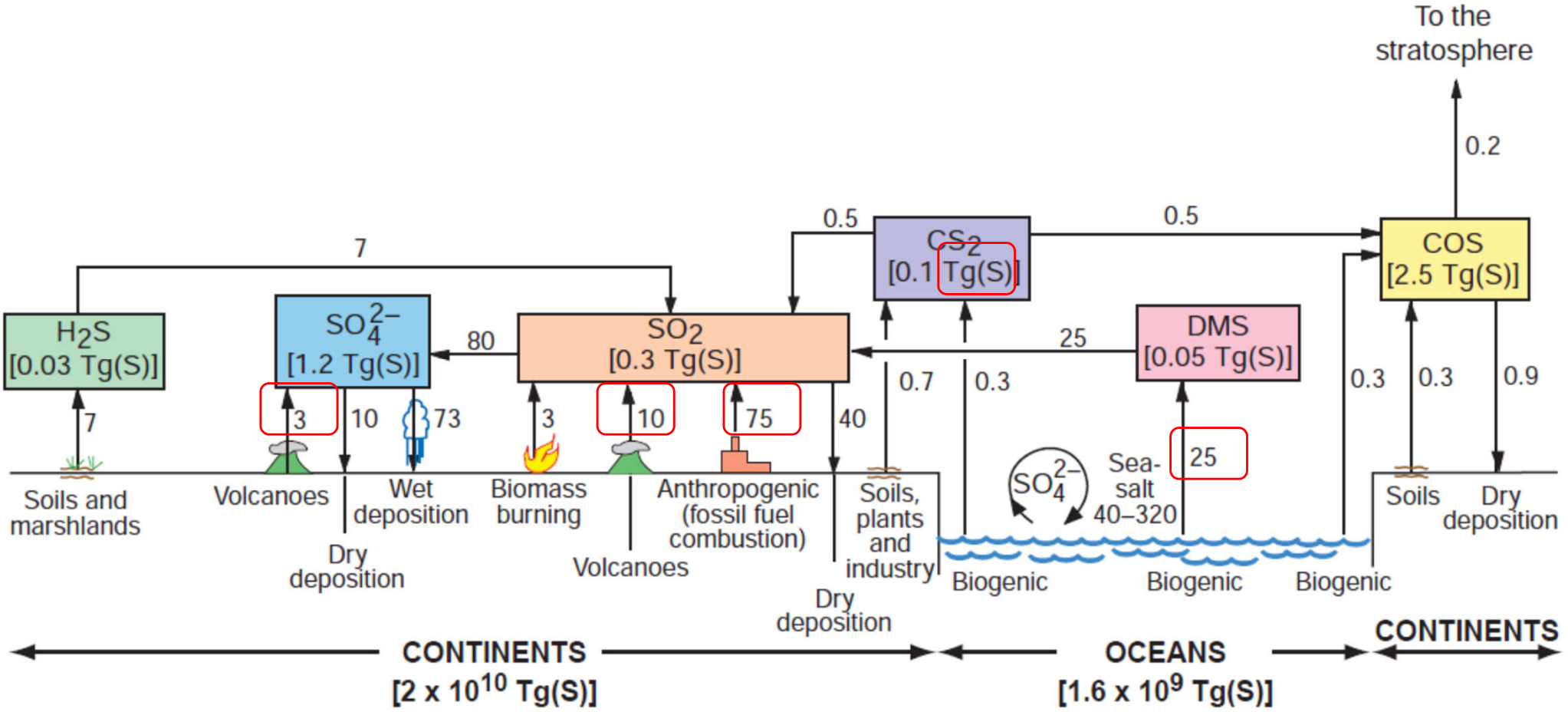


Fig. 5.15 As for Fig. 5.14 but for sulfur-containing species in the troposphere. Fluxes are in Tg(S) per year. For clarity, wet and dry removal are shown only over the continents, although they also occur over the oceans. [Adapted from P. V. Hobbs, *Introduction to Atmospheric Chemistry*, Camb. Univ. Press, 2000, p. 150. Reprinted with the permission of Cambridge University Press.]

Wulkany: 13 Tg
Spalanie paliw: 75
Dimethylsulphide: 25

Bilans ozonu

Archibald, A.T., et al. 2020. Tropospheric Ozone Assessment Report: A critical review of changes in the tropospheric ozone burden and budget from 1850 to 2100. *Elem Sci Anth*, 8: 1. DOI: https://doi.org/10.1525/elementa.2020.034

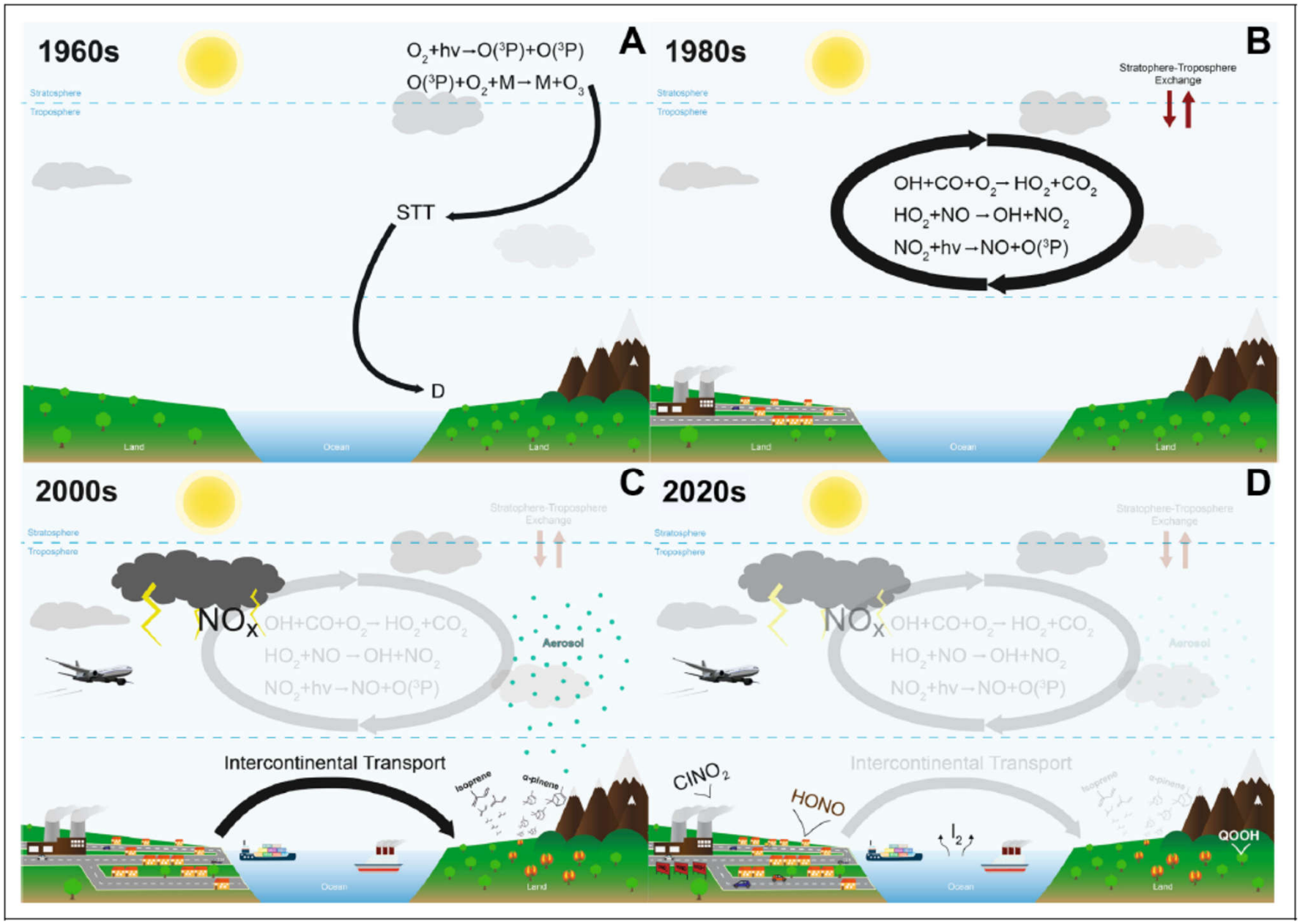


Figure 1. Schematic illustration of how our understanding of the chemical and physical processes controlling tropospheric ozone has evolved. The panels highlight the key processes identified in the different time periods. The labeling of dates in the subpanels (A–D) is indicative. DOI: https://doi.org/10.1525/elementa.2020.034.f1

Bilans ozonu

Archibald, A.T., et al. 2020. Tropospheric Ozone Assessment Report: A critical review of changes in the tropospheric ozone burden and budget from 1850 to 2100. *Elem Sci Anth*, 8: 1. DOI: https://doi.org/10.1525/elementa.2020.034

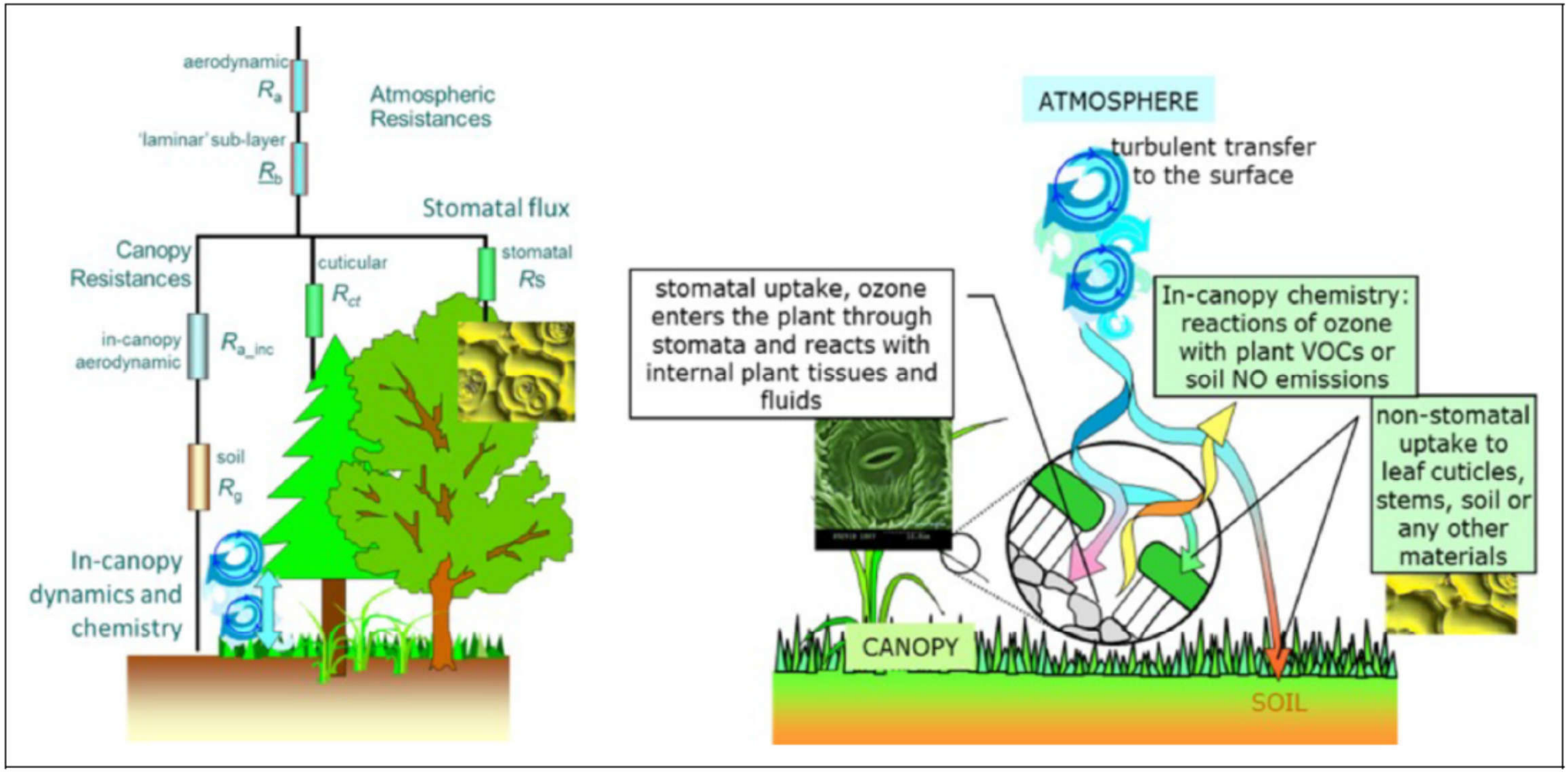


Figure 2. Pathways of ozone deposition on vegetated surfaces (with or without the resistance analogue used to quantify and model the processes). DOI: https://doi.org/10.1525/elementa.2020.034.f2

Bilans ozonu

Archibald, A.T., et al. 2020. Tropospheric Ozone Assessment Report: A critical review of changes in the tropospheric ozone burden and budget from 1850 to 2100. *Elem Sci Anth*, 8: 1. DOI: https://doi.org/10.1525/elementa.2020.034

3.1. The photochemical formation mechanism of tropospheric ozone

It is well established that tropospheric ozone is mainly a secondary photochemical product that results from the photolysis of NO_2.

(R1a) $RO_2/HO_2 + NO \rightarrow NO_2 + RO/OH$
(R1b) $RO_2 + NO + M \rightarrow RONO_2 + M$ (minor)
(R2) $NO_2 + h\nu \rightarrow NO + O(^3P)$ ($\lambda \leq 400$ nm)
(R3) $O_2 + O(^3P) + M \rightarrow O_3 + M$

RO_2/HO_2 are organic peroxy radicals (R refers to an alkyl, aryl, or alkenyl group) and the hydroperoxy radical, respectively. These compounds are key intermediates in the production of ozone in the troposphere (see Section 5.5 for more details) as they convert NO into NO_2 without destroying ozone. They are formed from the oxidation of VOCs and CO with OH. $RONO_2$ represent organic nitrates that can act as a local sink of oxidants and a reservoir for ozone precursors. The OH radical is the primary oxidant in the troposphere, for which ozone itself is the primary source via reactions R4 and R5.

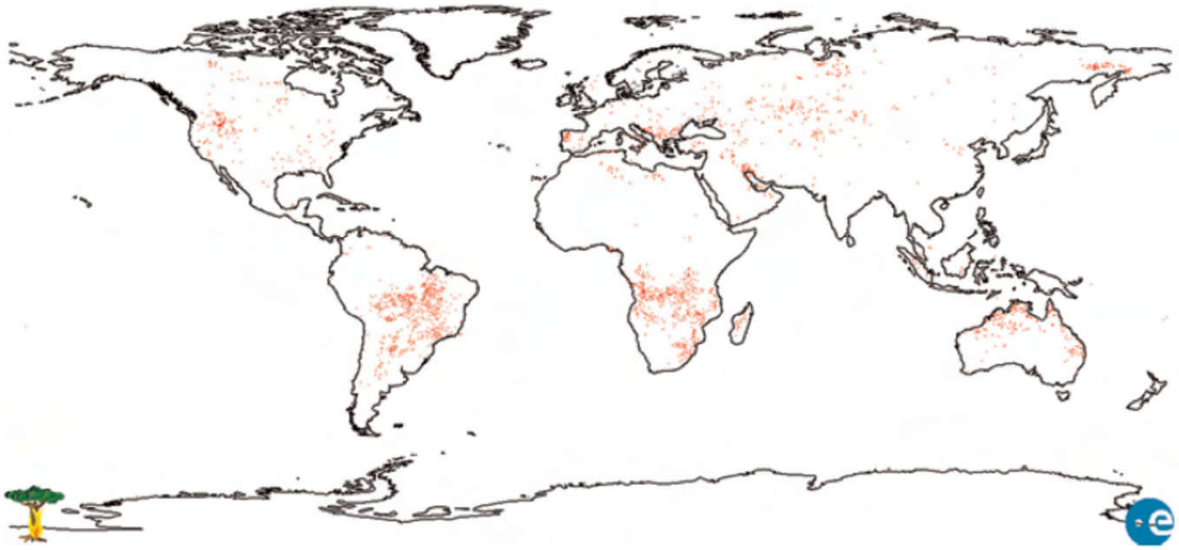
(R4) $O_3 + h\nu \rightarrow O(^1D) + O_2$ ($\lambda \leq 315$ nm)
(R8) $HO_2 + O_3 \rightarrow OH + 2\ O_2$
(R9) $OH + O_3 \rightarrow HO_2 + O_2$
(R10) $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
(R11) $HO_2 + RO_2 \rightarrow ROOH + O_2$

In addition to these chemical sinks of ozone, there are a number of physical sinks of ozone—deposition to surfaces (see Section 2.1) and uptake (including of oxidant reservoirs) onto particles (see Section 5.6)—that remove ozone from the troposphere.

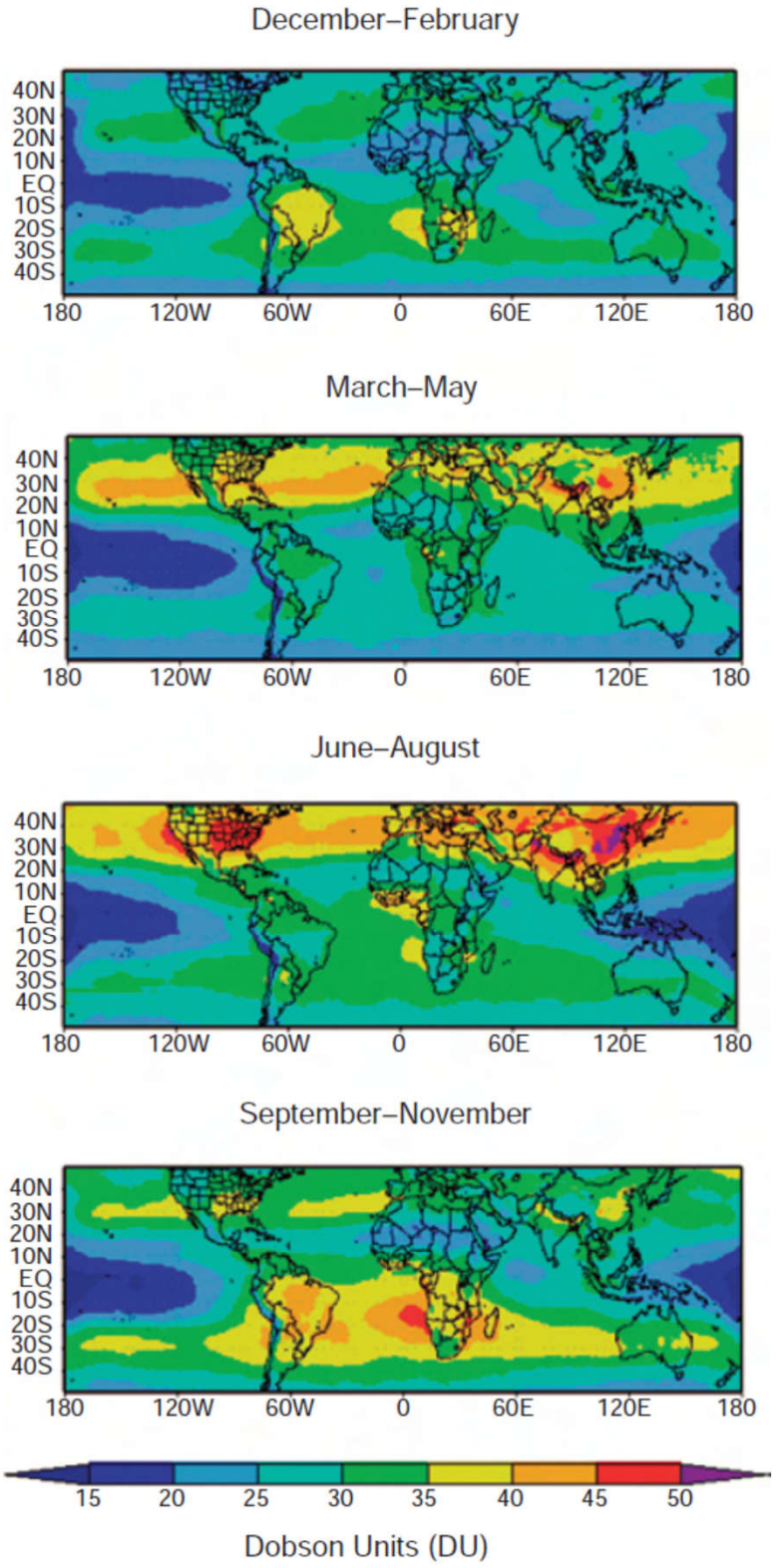
Owing to the fast photolysis of NO_2 during the day, reactions that convert NO into NO_2 without the consumption of ozone are considered as ozone producing reactions (i.e., R12a), and reactions that convert NO_2 into other members of the NO_z family (the molecules of oxidized nitrogen [NO_y] excluding NO and NO_2) are considered as ozone destroying (e.g., R7 and R12b). Experimental evidence for a minor, but potentially important, channel of the reaction between HO_2 and NO producing nitric acid ($HONO_2$; channel 12b) has been reported (Butkovskaya et al., 2005, 2007, 2009). The main sink of $HONO_2$ is surface deposition.

(R12a) $HO_2 + NO \rightarrow HO + NO_2$
(R12b) $HO_2 + NO + M \rightarrow HONO_2 + M$

Ozon w troposferze



Global distribution of fires detected by satellite in September 2000. [Image courtesy of European Space

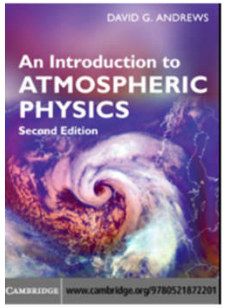


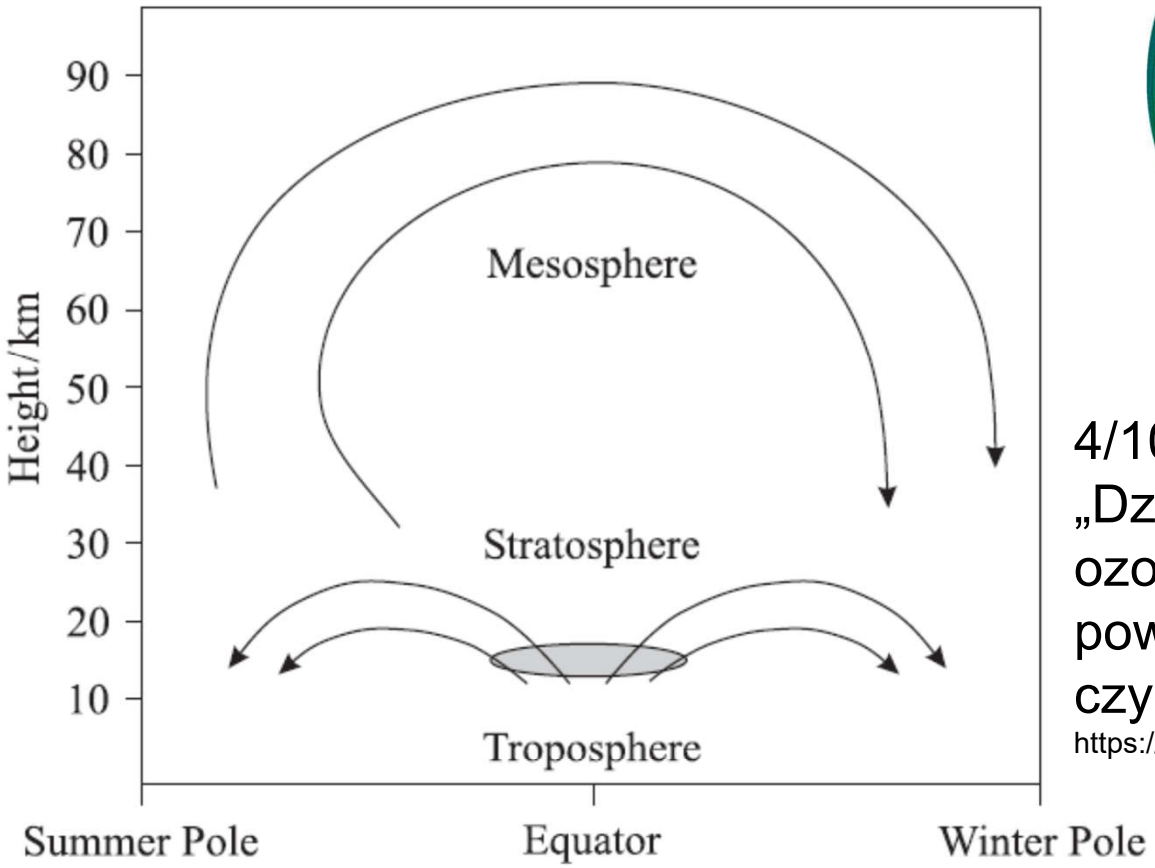
Smuga ozonu znad Afryki (wiosną) pochodzi ze spalania biomasy

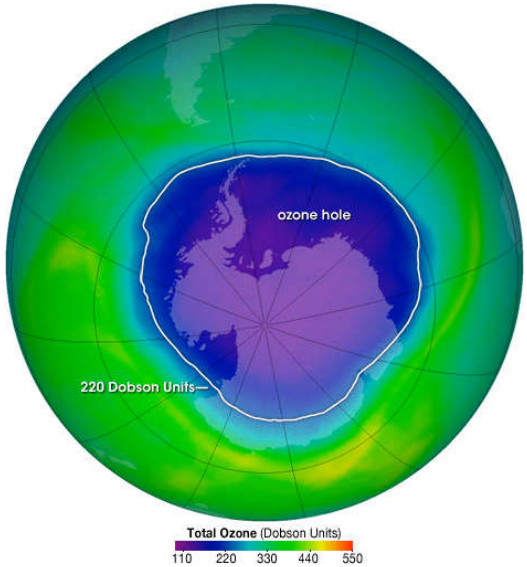
Podobna smuga nad Azją i Ameryką Płn., latem

Atmos. Chem. Phys. 3 895 (2005)

Powstawanie i transport ozonu





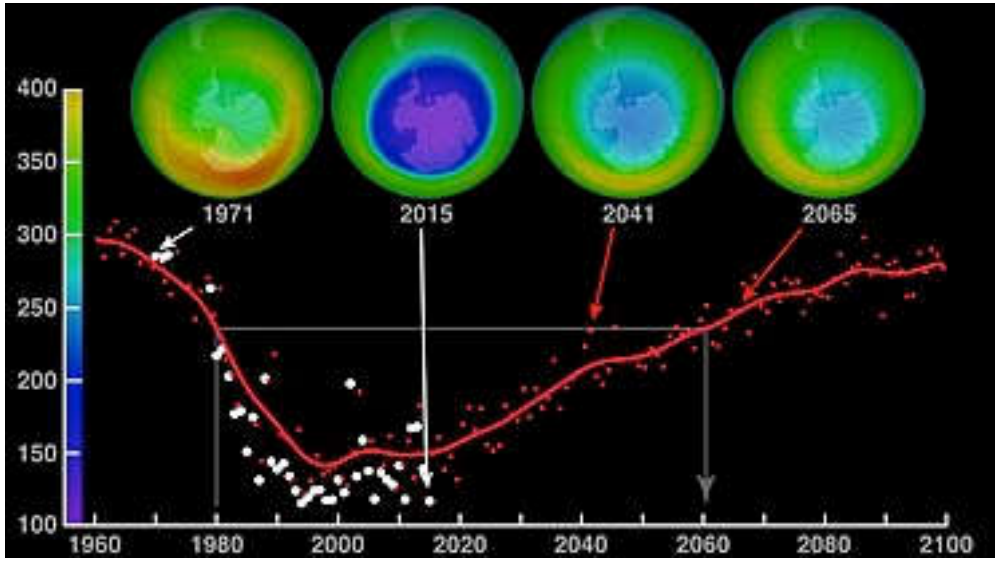


4/10/2004
„Dziura” ozonowa oznacza, że ozonu jest mniej tam, gdzie powinien być jego rezerwuar, czyli nad Antarktydą
https://ozonewatch.gsfc.nasa.gov/facts/hole_SH.html

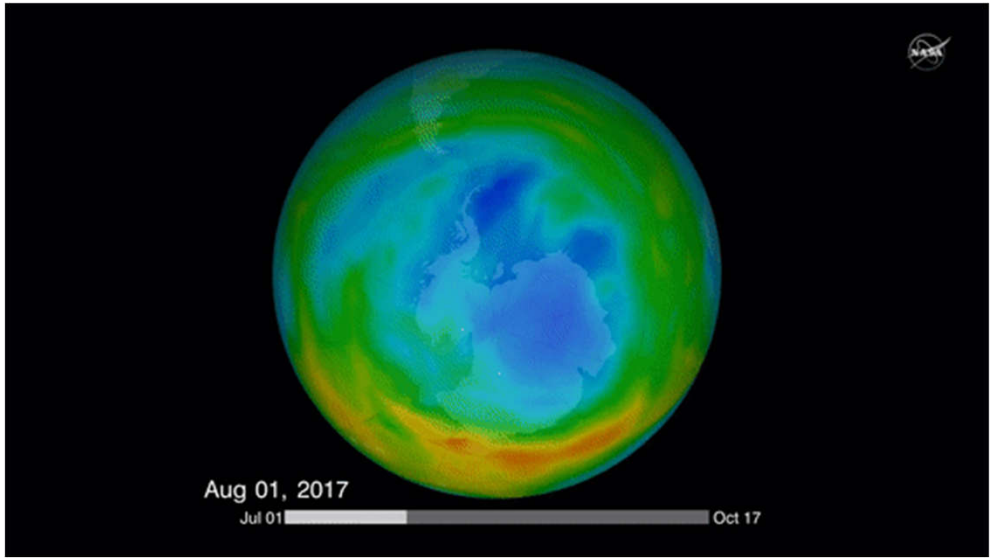
A schematic plot of the Brewer–Dobson circulation (lower four arrows, in the stratosphere) and the solstitial mesospheric circulation (upper two arrows). The shaded ellipse indicates the approximate position of the 200 K isotherm near the equatorial tropopause, i.e. the 'cold trap' identified by Brewer (1949).

Ozon, powstający w 200 K w dolnej stratosferze nad równikiem (pułapce) jest transportowany ku biegunom; poprzez mezosferę cyrkuluje między biegunami (pokazana cyrkulacja w czasie przesilenia letniego)

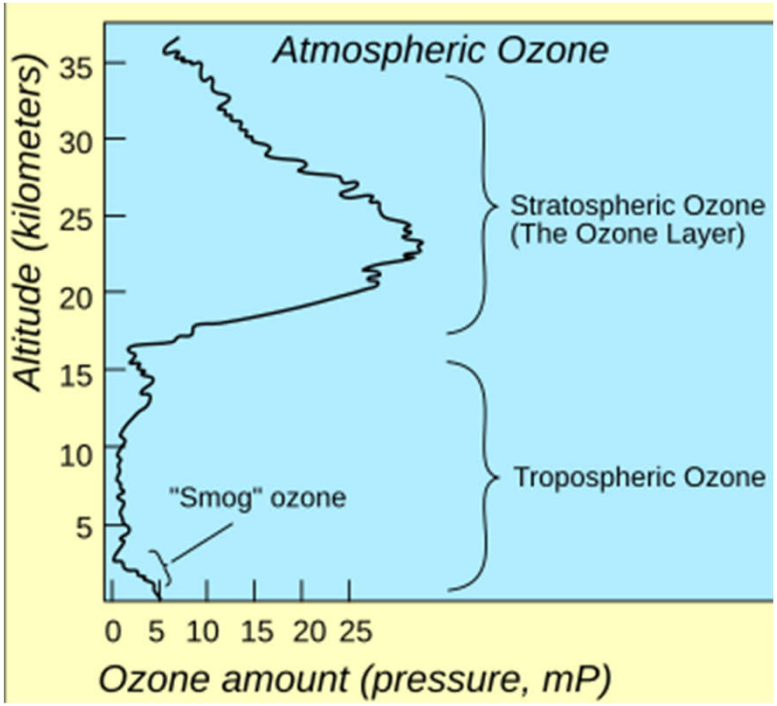
„Dziura” ozonowa nadal istnieje, ale powoli się zabliźnia



https://upload.wikimedia.org/wikipedia/commons/thumb/4/4d/Ozone_hole_recovery.jpg/555px-Ozone_hole_recovery.jpg

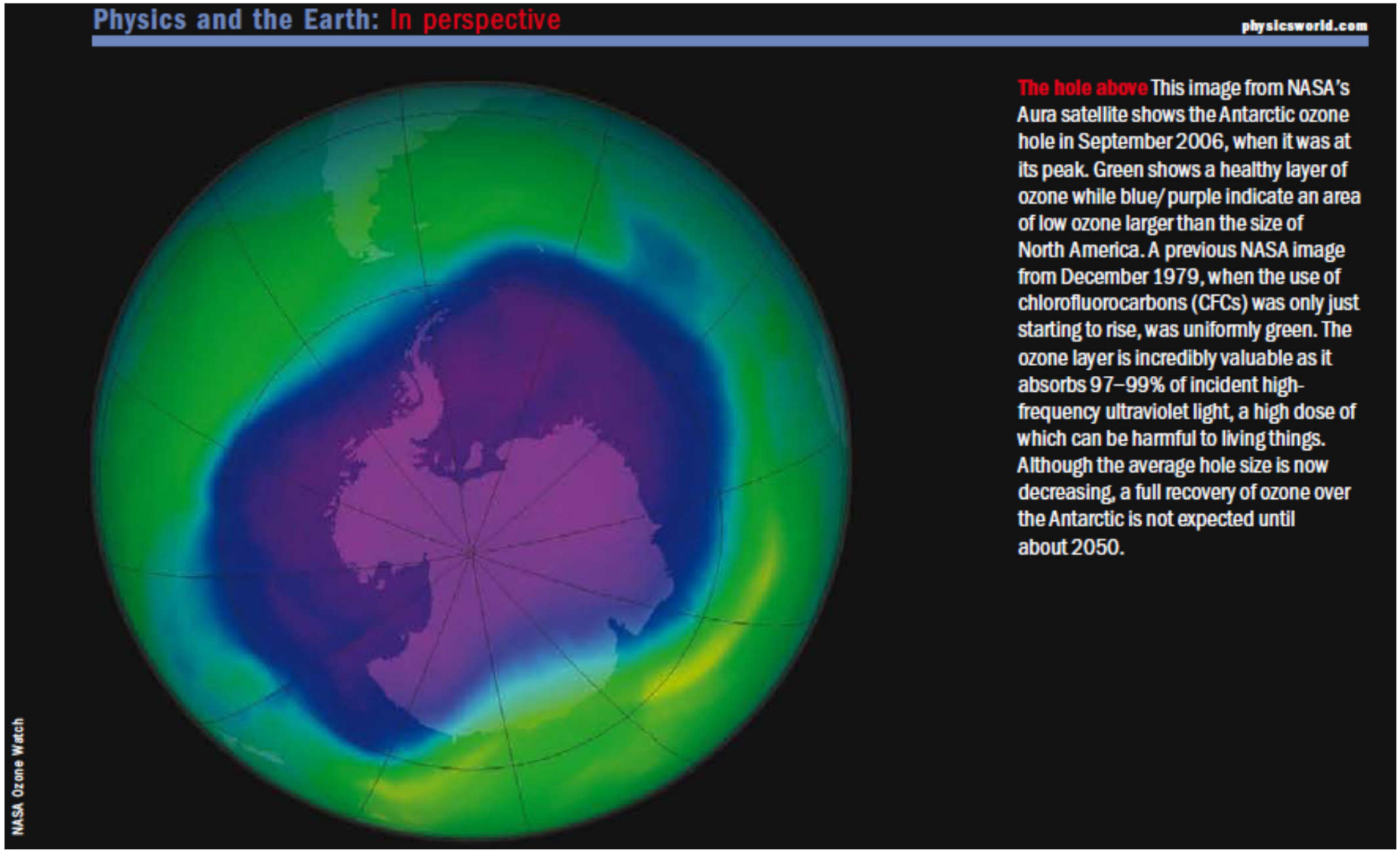


https://www.nbcnews.com/mach/science/good-news-about-ozone-hole-even-better-you-think-ncna835971



„Scałkowanie” ciśnienia parcjalnego ozonu (max 25 mPa) po grubości warstwy (ok. 10km) jest równoważne grubości warstwy około **2,5 mm** pod ciśnieniem atmosferycznym (10^5 Pa)

Dziura ozonowa

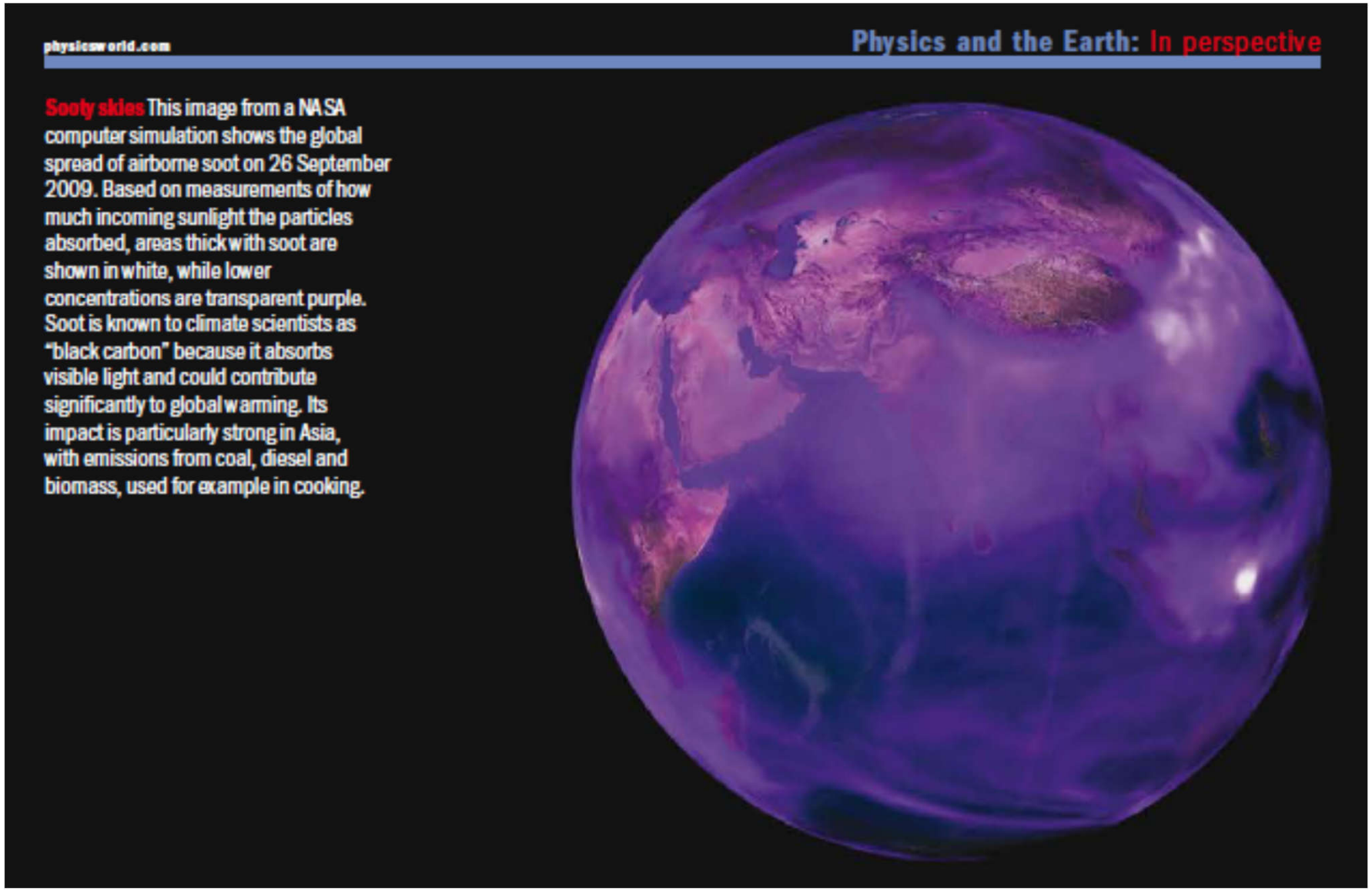


Ozon wymaga niskich temperatur do jego stabilizacji: powstaje więc głównie w rejonie biegunów. Aerozole używane w kosmetykach (CFC) spowodowały katalityczny rozkład Ozonu. Dziura powoli zabliźnia się, ale potrwa to jeszcze dziesiątki lat.

Półwysep Iberyjski (i stratosfera) nocą 4.12.2011 roku

Delta Nilu nocą: „hałas” świateł miast widać z kosmosu

Antroposfera: sadza



Zapylenie miast chińskich (i do niedawna japońskich) jest takie, że Słońce widać tam tylko przez kilka dni w roku.

Czym ma tak naprawdę oddychamy?

Trento,
14.03.2003, godz. 8:00

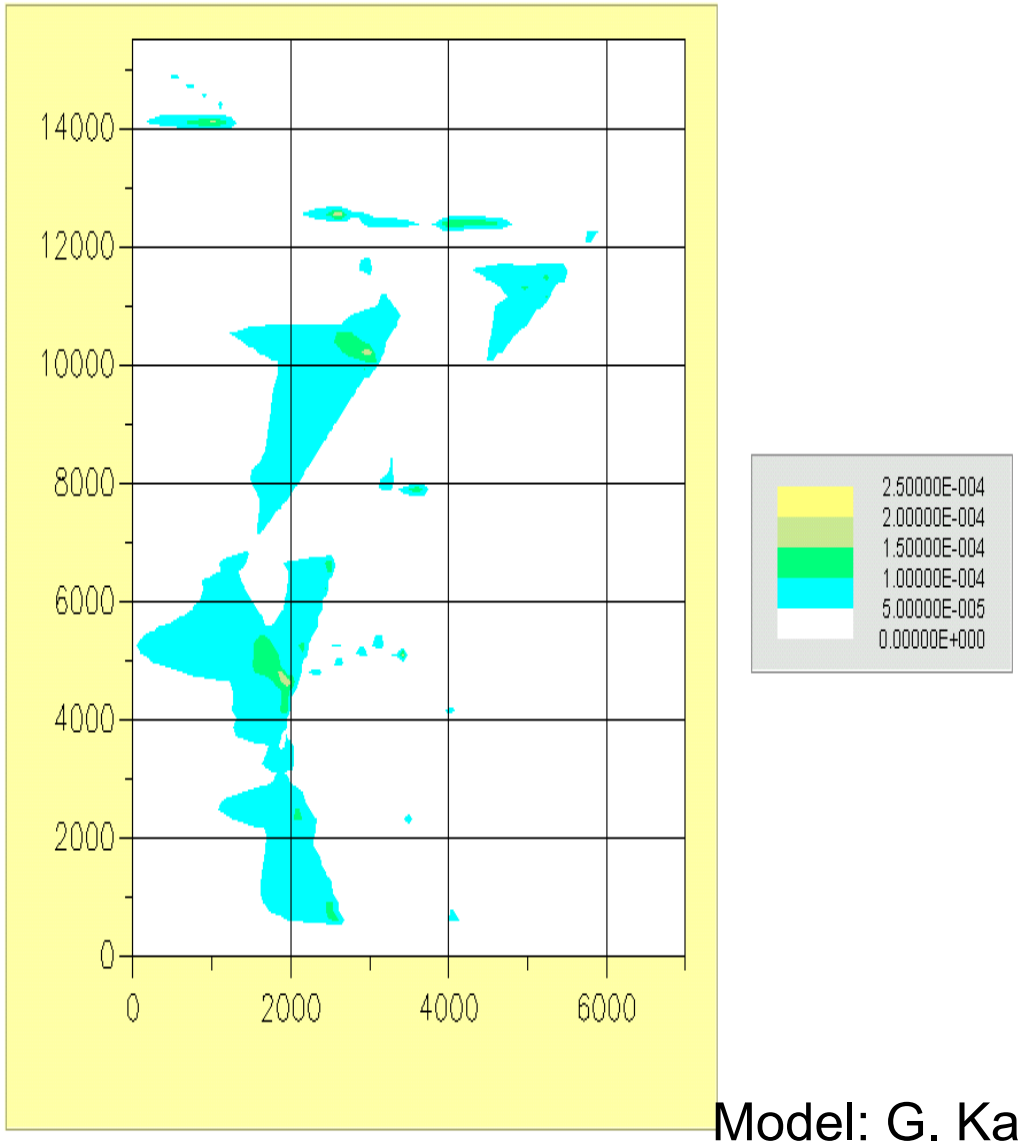
Foto GK

Zanieczyszczenie atmosferyczne (lokalne):

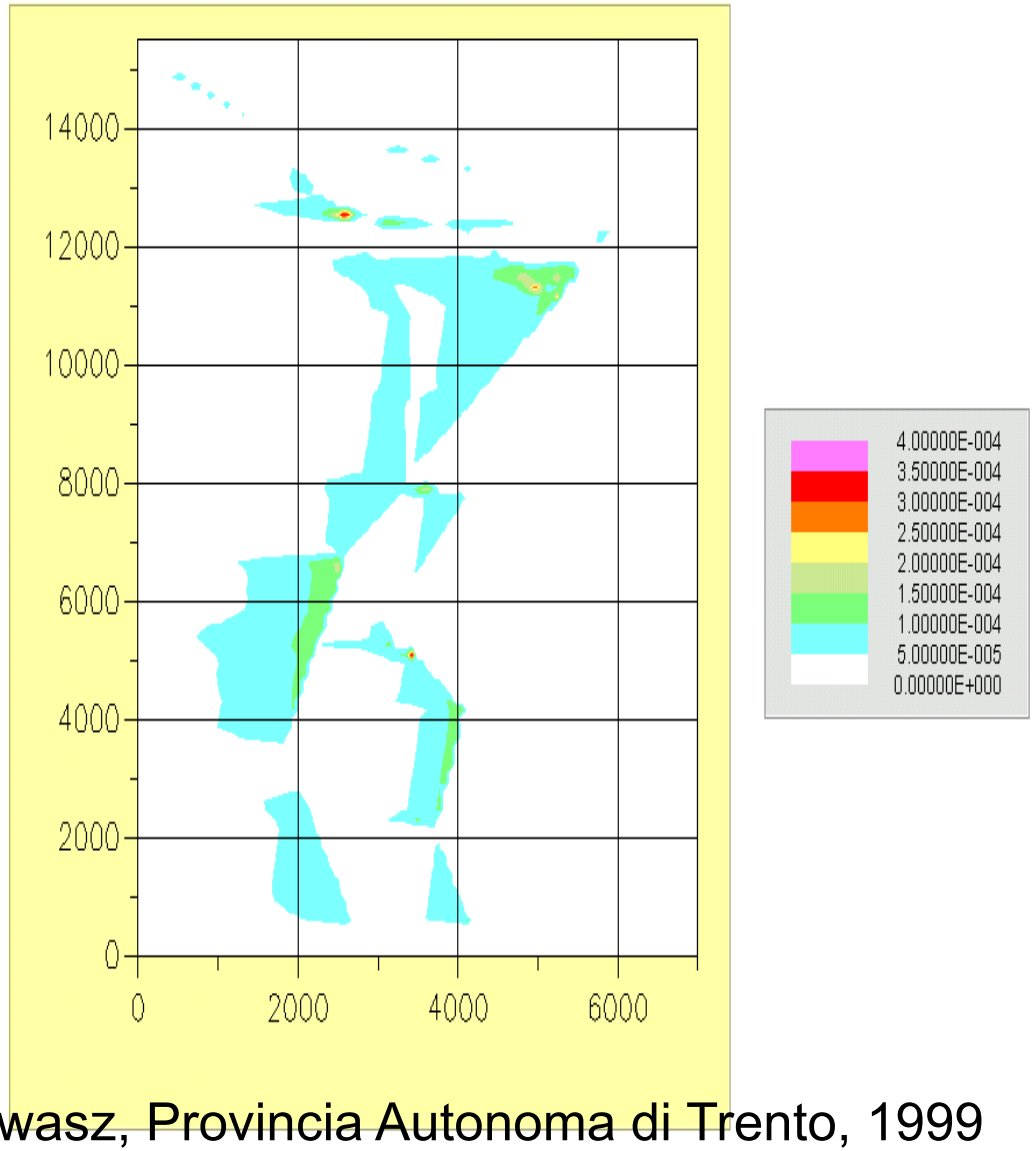
- Tlenek węgla CO 30 mg/m^3
- Mikropyły (PM10) 150 $\mu g/m^3$
- Tlenki azotu (NO, NO_2) 200 $\mu g/m^3$
- Dwutlenek siarki (SO_2) 15 mg/m^3
- ozon O_3 180 $\mu g/m^3$ (dla roślin 150 $\mu g/m^3$)
- Węglowodory (benzen) 15 $\mu g/m^3$

Modelowanie zanieczyszczeń = prewencja

Viabilità attuale

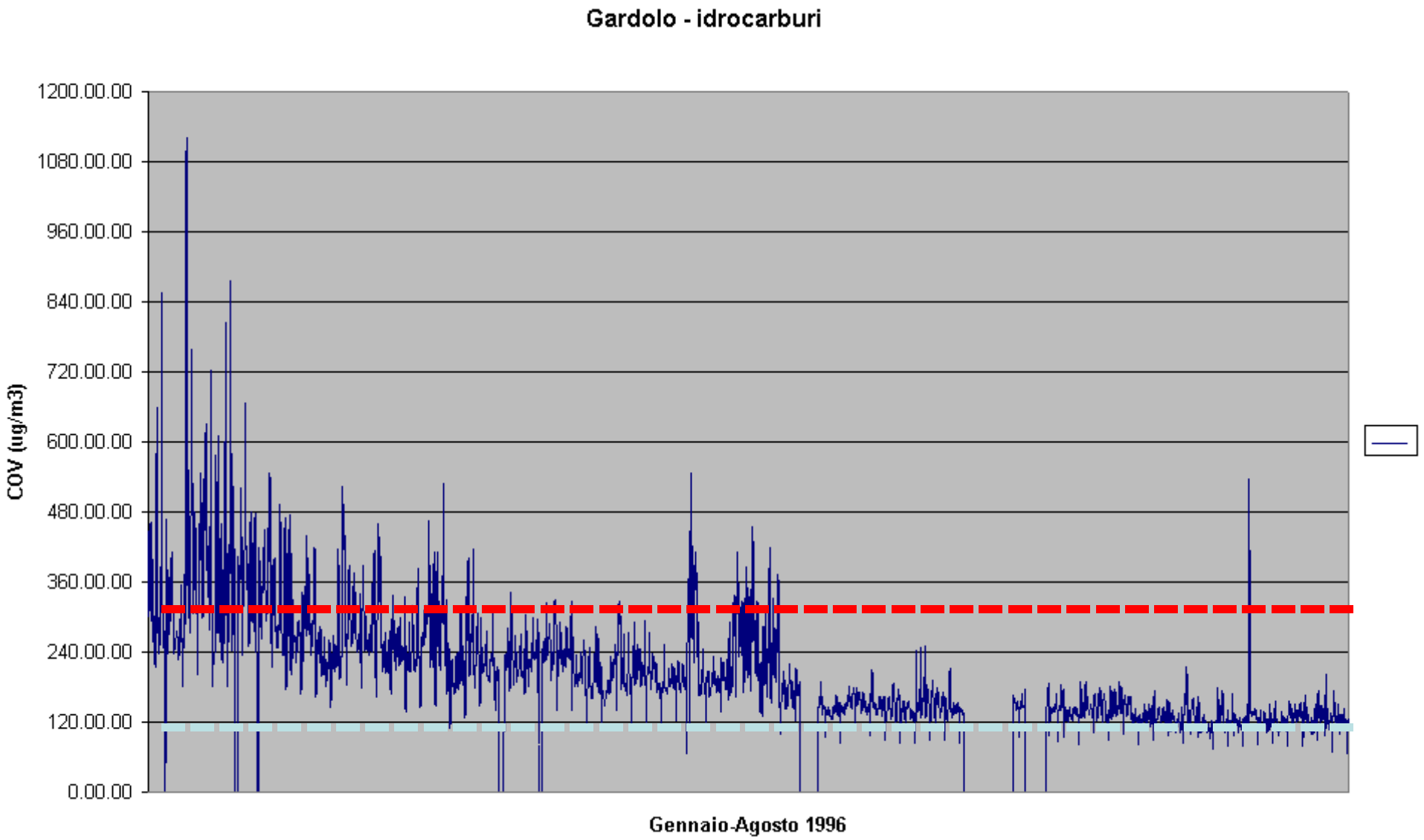


Traforo Mezzolombardo



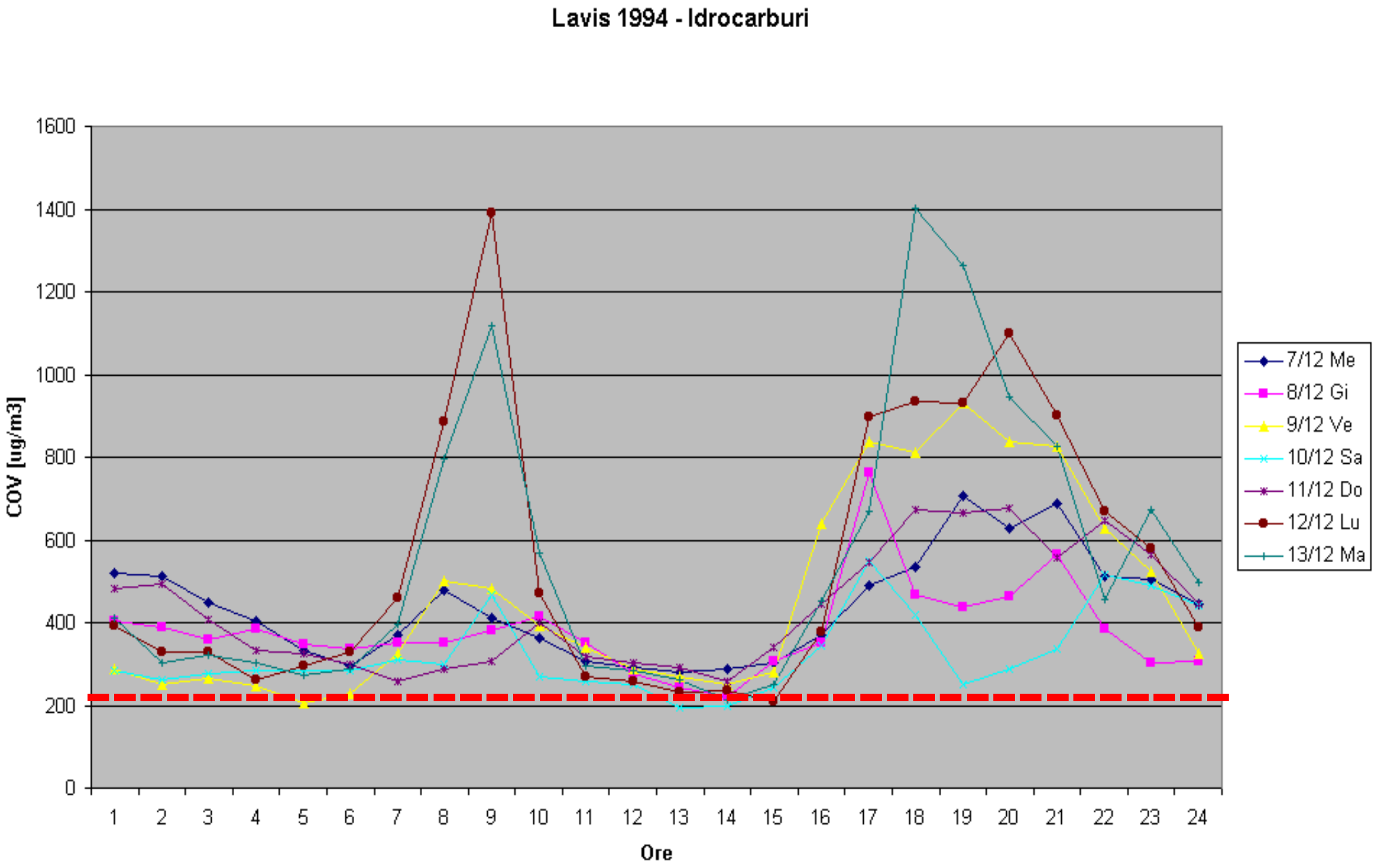
Model: G. Karwasz, Provincia Autonoma di Trento, 1999

Zanieczyszczenie lokalne (węglowodory)



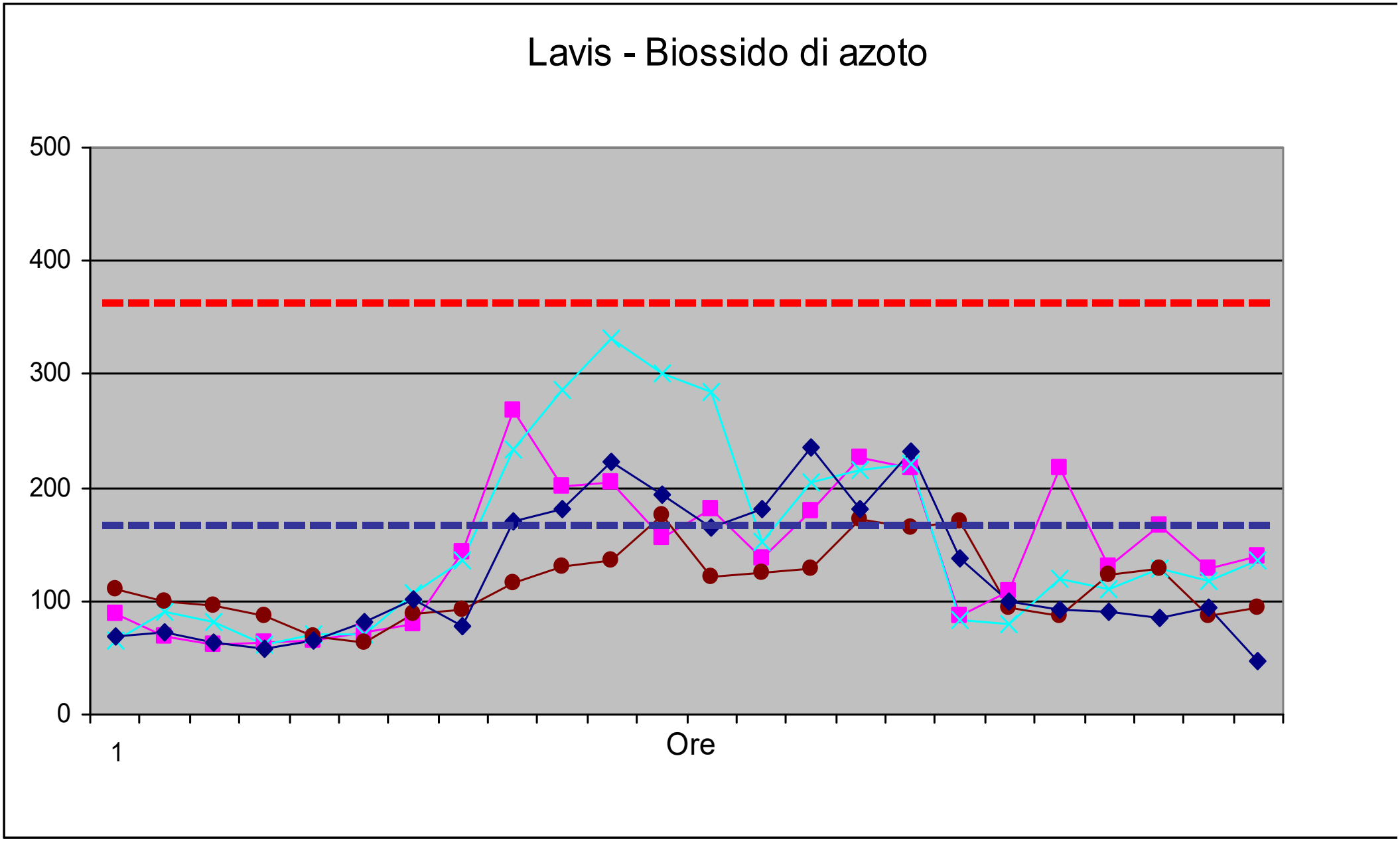
Analiza: GK

Zanieczyszczenie lokalne (węglowodory – ruch drogowy)



Analizal: G. Karwasz, Provincia Autonoma di Trento, 1999

Zanieczyszczenie localne – dwutlenek azotu



Analiza: G. Karwasz, Provincia Autonoma di Trento, 1999

Londyn, 2002

G. Karwasz, Rapporto per Comune di Trento, 2002
Foto: Maria Karwasz

XXV-lecie PRL

G. Karwasz, Wykład otwarty, UMK, 2017

Polska ma najbardziej zanieczyszczone powietrze w UE

30 gru 14:07:44

Skomentuj 0 Podziel się 0

fot. wburris, flickr,cc

G. Karwasz, Wykład otwarty, UMK, 2017

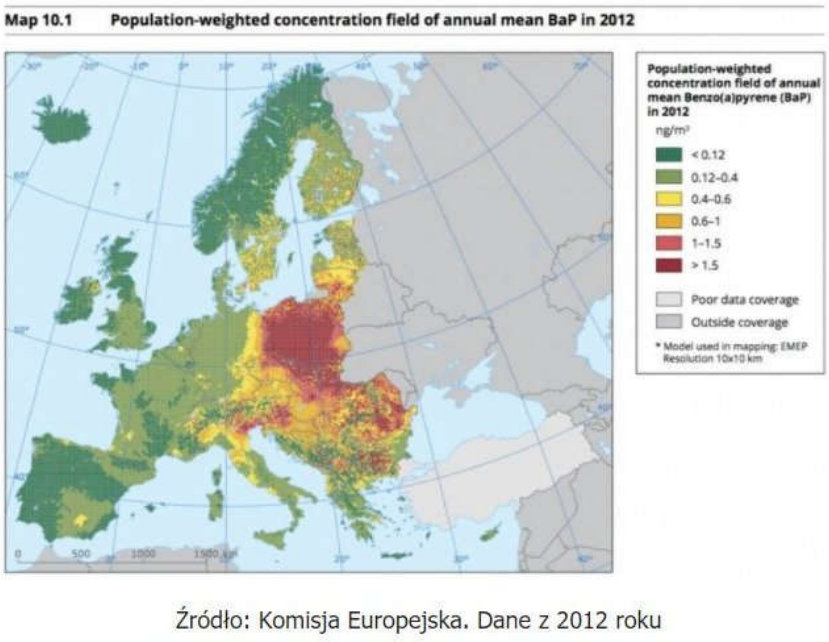
Polska od lat ma najbardziej zanieczyszczone powietrze w Unii Europejskiej - alarmuje NIK. Izba wskazuje, że

- https://www.forbes.pl/csr/polska-ma-najbardziej-zanieczyszczone-powietrze-w-ue/sfb3hlm

Eksport smogu miejskiego

FOCUS.pl

1/2



Źródło: Komisja Europejska. Dane z 2012 roku

Polska na czele krajów zatruwających powietrze w Unii Europejskiej

1/2. Polska na czele krajów zatruwających powietrze w Unii Europejskiej

Stężenie benzopirenów w powietrzu

„Polska w czołówce krajów zanieczyszczających powietrze w Europie”

Mapa pokazuje stężenia benzopirenu (rakotwórczego) pochodzącego ze spalania węgla.

Polska nie tylko produkuje ogromną ilość benzopirenu (średnie stężenie dziesięć razy powyżej dopuszczalnego limitu), ale także „eksportuje” go swobodnie do sąsiadów.

Polska: jakość powietrza (I)

Polska od lat ma najbardziej zanieczyszczone powietrze w Unii Europejskiej - alarmuje NIK. Izba wskazuje, że mimo iż samorządy wydawały pieniądze na walkę z zanieczyszczeniami, jakość powietrza, którym oddychamy, poprawiła się tylko nieznacznie

Najwyższa Izba Kontroli w opublikowanym w poniedziałek raporcie podkreśliła, że niespełnienie standardów jakości powietrza, które są określone w prawie unijnym (tzw. dyrektywa CAFE), może kosztować Polskę nawet 4 mld zł kary.

3. Kraków
…
10. Katowice

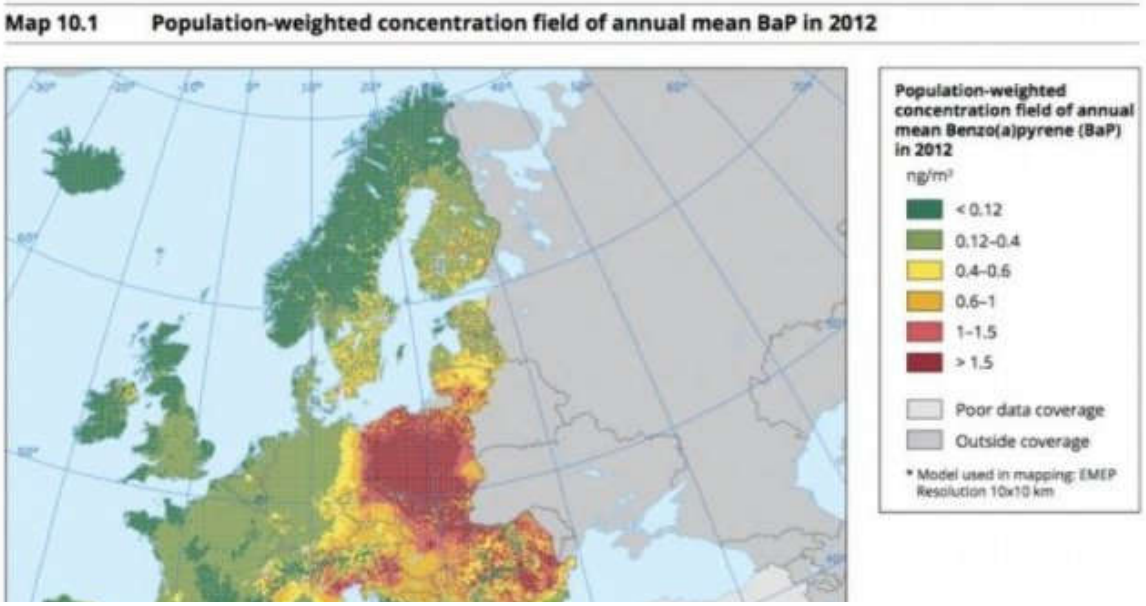
Izba powołała się na dane OECD, które wskazują, ze ponad 3,5 mln osób na świecie przedwcześnie umiera z powodu chorób wywoływanych **zanieczyszczonym powietrzem**. W Polsce szacuje się, że rocznie z tego powodu może tracić życie nawet 45 tys. osób.

"Niestety dane te, choć są szokujące, nie powinny dziwić, skoro Polska od lat ma najbardziej zanieczyszczone powietrze w całej Unii. Według informacji Europejskiej Agencji Środowiska aż 6 polskich miast znalazło się w pierwszej dziesiątce miast europejskich z największą liczbą dni w roku, w których przekroczono dobowe dopuszczalne stężenie pyłu PM10 (pozostałe cztery miasta są w Bułgarii)" - dodano w raporcie.

Polska: jakość powietrza (II)

FOCUS.pl

1/2



Polska na czele krajów zatruwających powietrze w Unii Europejskiej

1/2. Polska na czele krajów zatruwających powietrze w Unii Europejskiej

Stężenie benzopirenu w powietrzu

NIK wskazała, że największym problemem dla jakości powietrza w Polsce jest ponadnormatywne stężenie pyłu zawieszonego (PM10 i PM2,5) oraz benzo(a)pirenu (B(a)P). "Wysokie stężenie pyłu zawieszonego powoduje i pogłębia choroby płuc i układu krążenia. Z kolei benzo(a)piren jest związkiem silnie rakotwórczym. Tymczasem we wszystkich kontrolowanych miastach w 2013 r. dopuszczalne stężenie benzo(a)pirenu przekroczone zostało średnio o 500 proc. Najwyższe stężenie B(a)P odnotowano w Nowym Sączu - limity przekroczone jedenastokrotnie, a w Głubczycach (w woj. opolskim) dziesięciokrotnie. Z kolei w czterech miastach (Kraków, Nowy Sącz, Katowice i Dąbrowa Górnicza) przekroczone zostało średnioroczne stężenie PM10. W skali kraju w latach 2010-2013 przekroczono dopuszczalne poziomy pyłu PM10 w ponad 75 proc. wszystkich stref, w których dokonuje się oceny jakości powietrza, a w przypadku benzo(a)pirenu w ok. 90 proc. stref" - czytamy w raporcie.

Benzo-piren a rak

exposure (Maynard et al., 1997).

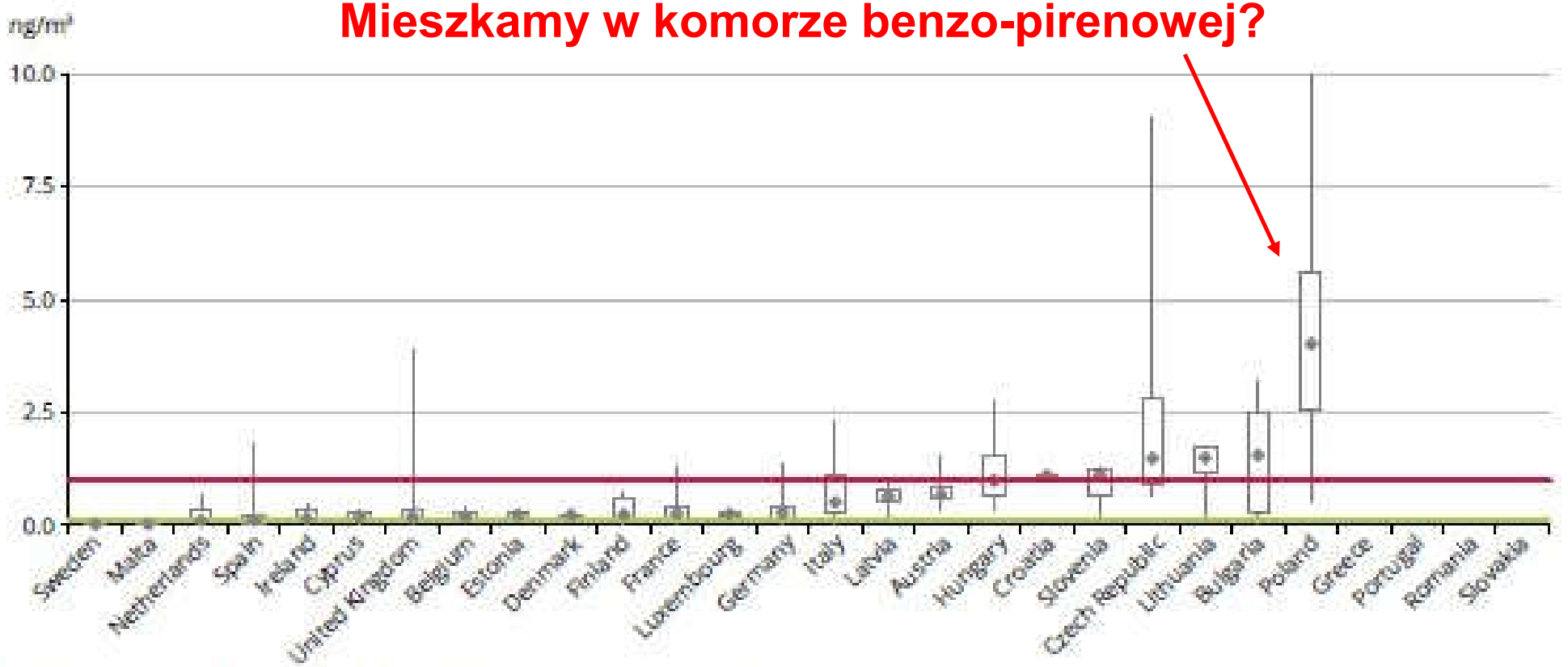
PAH=poli-aromatic-hydrocarbons

The UK Expert Panel on Air Quality Standards (EPAQS) used the scientific expert judgment approach to set the UK PAH standard for ambient air. EPAQS considered the PAH mixture described in an epidemiological study in an aluminum smelter in Canada, where high exposures were linked to lung cancers (Armstrong et al., 1994), as the best starting point for the derivation of the standard. Armstrong et al. (1994) identified that an exposure to of a mixture of PAH compounds represented by 0.25–2.5 μg/m^3 BaP during a working life (40 years) was associated with a 50% increase in the risk of lung cancer. The lower bound of this range, 0.25 μg/m^3 of BaP, was taken as representing the lowest observed adverse effect level (LOAEL). Three safety factors of 10 were used to account for (a) moving from a LOAEL to a no observed adverse effect level (NOAEL), (b) extrapolating from a working life exposure to an entire lifetime exposure, and (c) accounting for the range of sensitivity to carcinogens likely to exist in the general population. Hence, EPAQS selected the value of 0.25 ng/m^3 of BaP as the UK air quality standard (EPAQS, 1999).

Benzopiren w Polsce: 4 ng/m^3

Map 10.1 **Population-weighted concentration field of annual mean BaP in 2012**

Figure 6.1 **Attainment situation for BaP in 2013 in the EU-28**



Notes: The graph is based on the annual mean concentration values for each Member State. For each country, the lowest, highest and median values (in ng/m³) at the stations are given. The rectangles give the 25 and 75 percentiles. At 25% of the stations, levels are below the lower percentile; at 25% of the stations, concentrations are above the upper percentile. The target value set by EU legislation is marked by the red line. The estimated air quality reference level is marked by the green line.

Source: Based on Air Quality e-reporting database (EEA, 2015a).

Reference textbooks

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- P. Atkins, J. de Paula, *"Elements of Physical Chemistry"* OUP 2009 (or any other edition)

Available in the Mesiano (or Povo1) Library
Thanks to dr Daniela Ascenzi