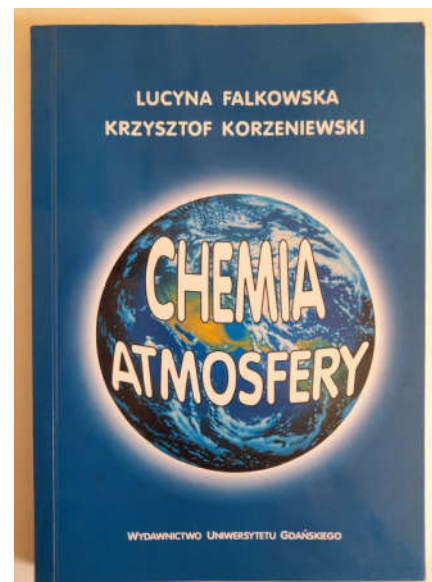
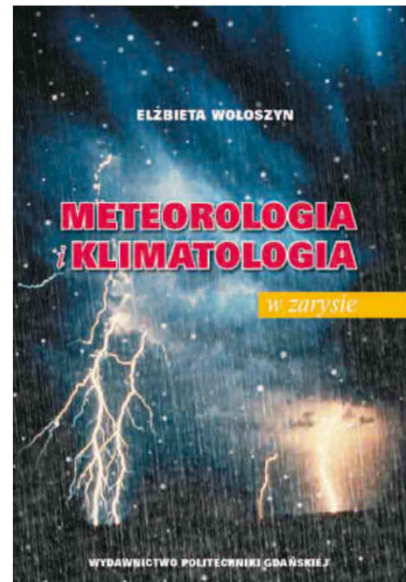
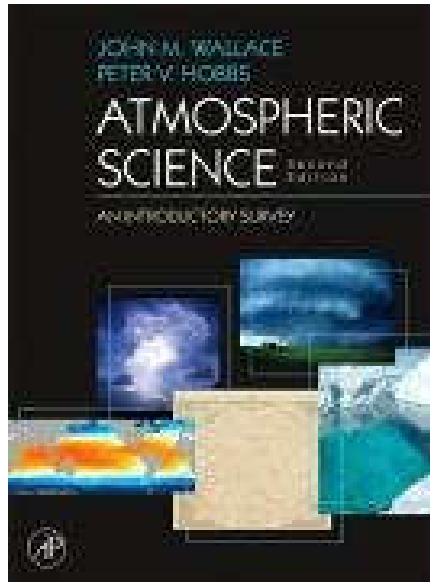


Atmosfera – chemia

Grzegorz Karwasz

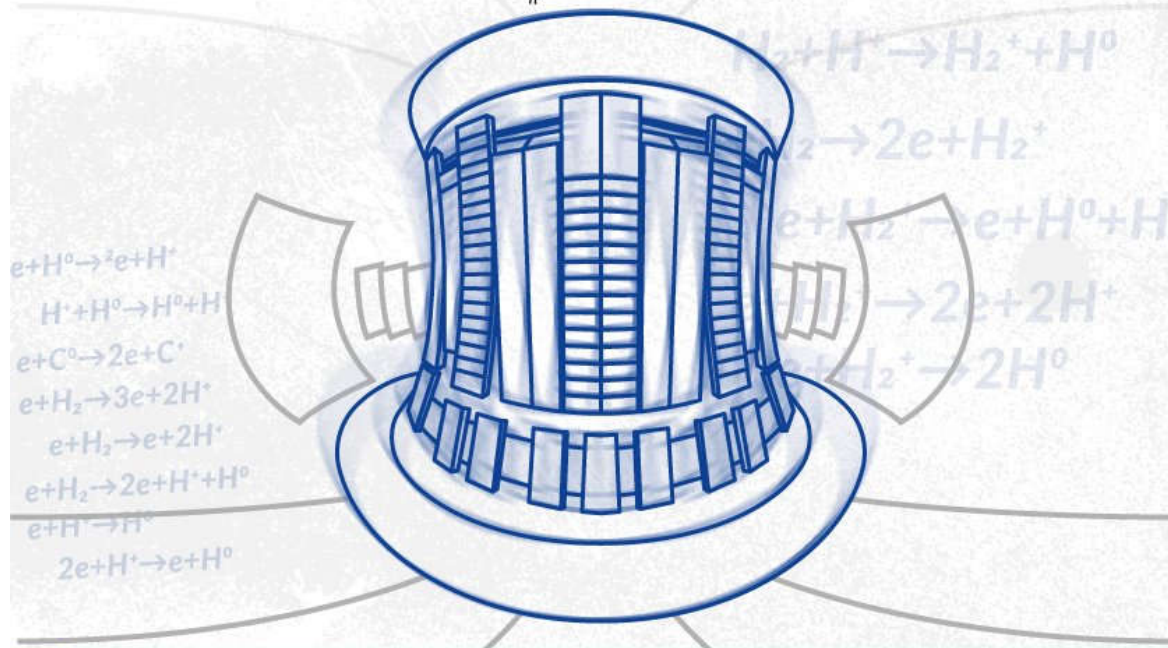
Wykład 9

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





$$\sigma = \sum_n 4\pi a_0^2 \xi_n \left(\frac{R}{I_n}\right)^2 \frac{1}{t+u_n+1} \left\{ 1 - \frac{1}{t} + \frac{\ln t}{2} \left(1 - \frac{1}{t^2}\right) - \frac{\ln t}{t+1} \right\}$$



Najprawdopodobniej w 2033 roku zabraknie w Polsce 33% energii elektrycznej, a w 2044 roku stężenie CO₂ w atmosferze przekroczy 440 części na milion, przez co średnia temperatura na globie podniesie się o 1,4°C.

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

III wykład z cyklu „Fizyka wokół nas”

Energia? Od ogniwa Volty do reaktora termojądrowego

prof. dr hab. inż. Grzegorz Karwasz

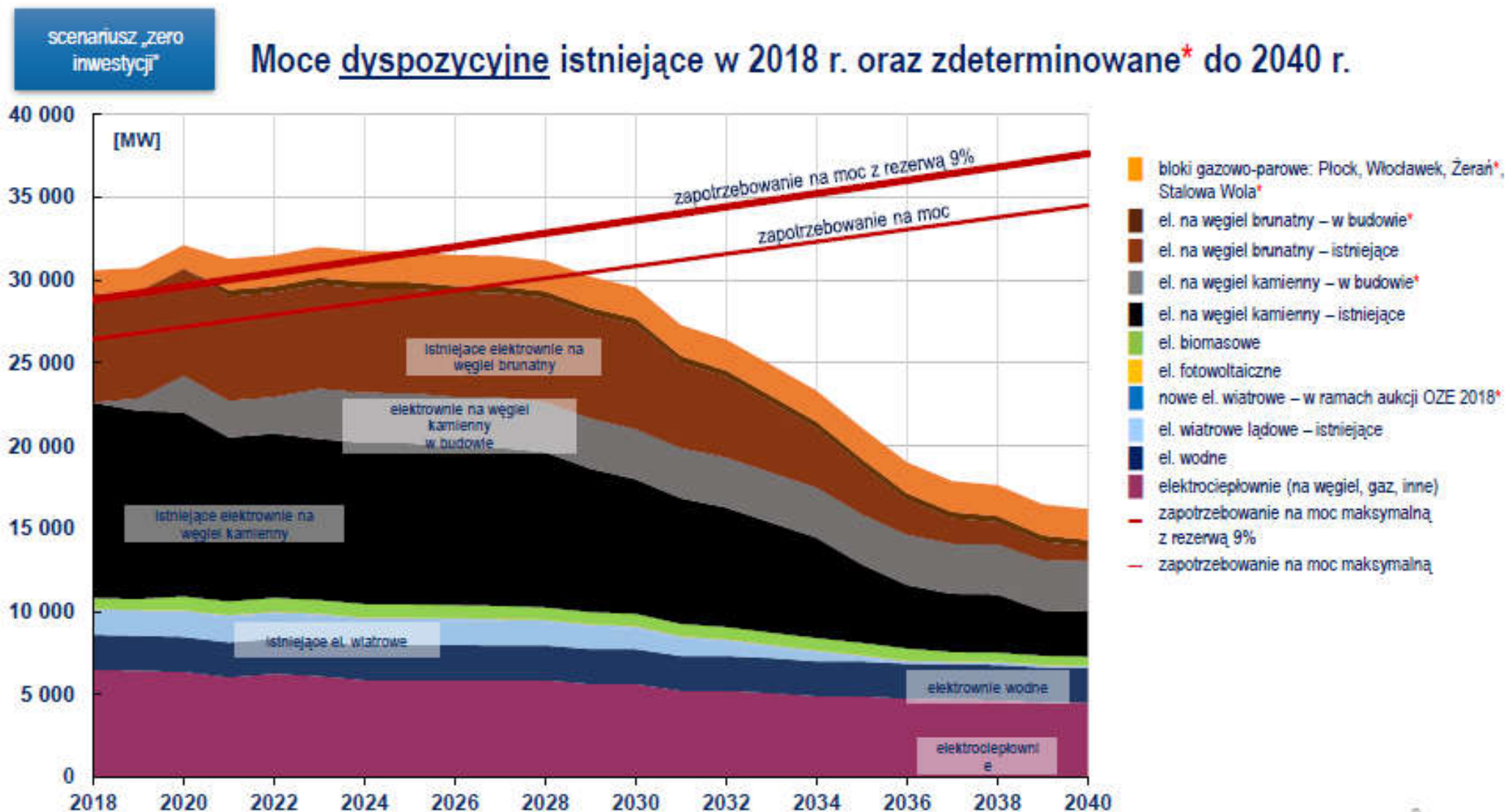
21.03.2019, godz. 17:15

Instytut Fizyki UMK, ul. Grudziądzka 5/7, Toruń

W prostych słowach o trudnych rzeczach....



Polityka energetyczna Polski (ME, 22.01.2019)



Rationale

A 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.

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

Václav Nevrlý et al.

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Population-Level Exposure to PM_{2.5}, NO₂, and O₃ in the United States



Sources and Variability of Greenhouse Gases over Greece



University of Trento
Master of Science in Environmental Meteorology
<https://international.unitn.it/environmental-meteorology>
A.A. 2023-24

Environmental Physical Chemistry

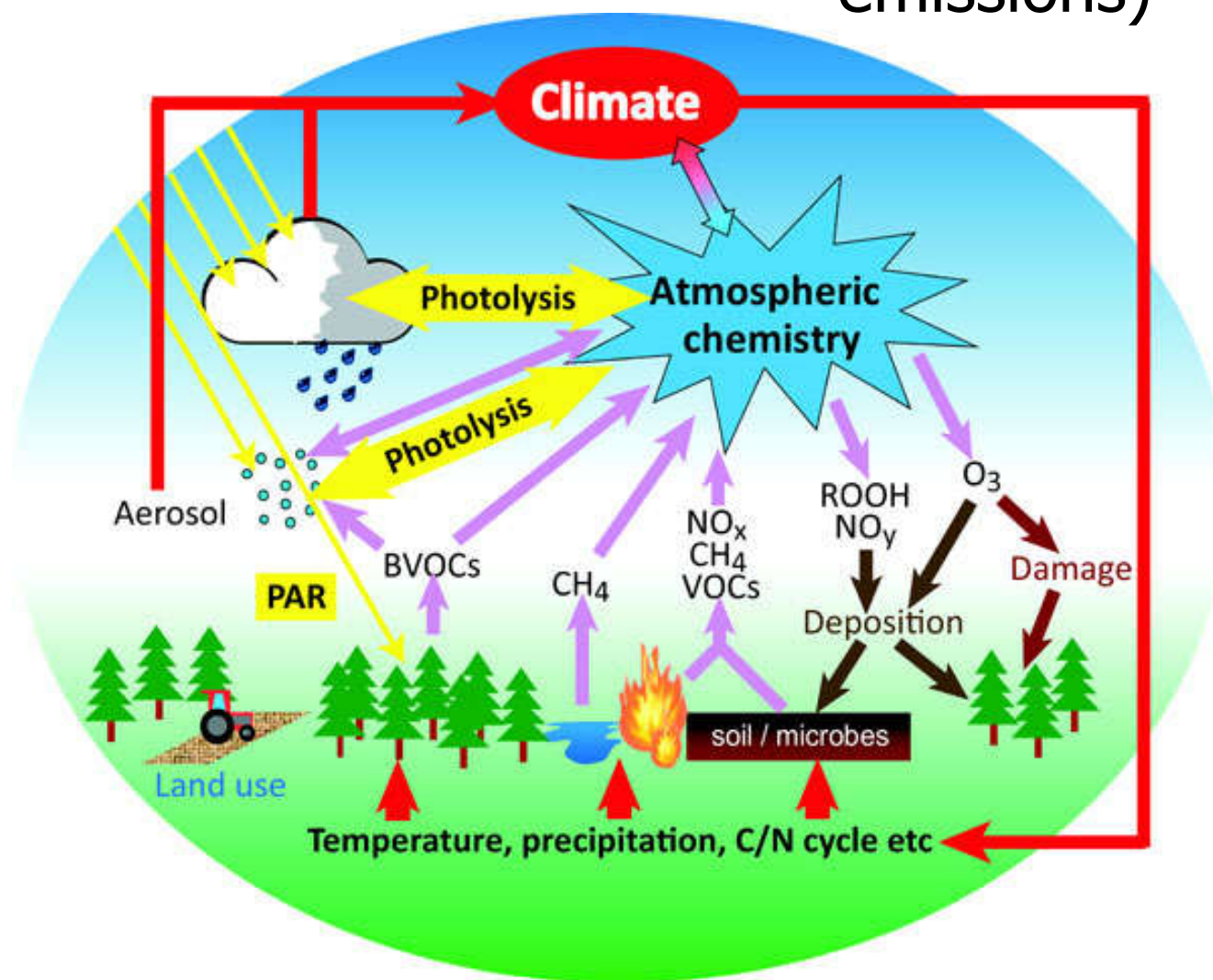
Light/matter interaction and basic principles of spectroscopy

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

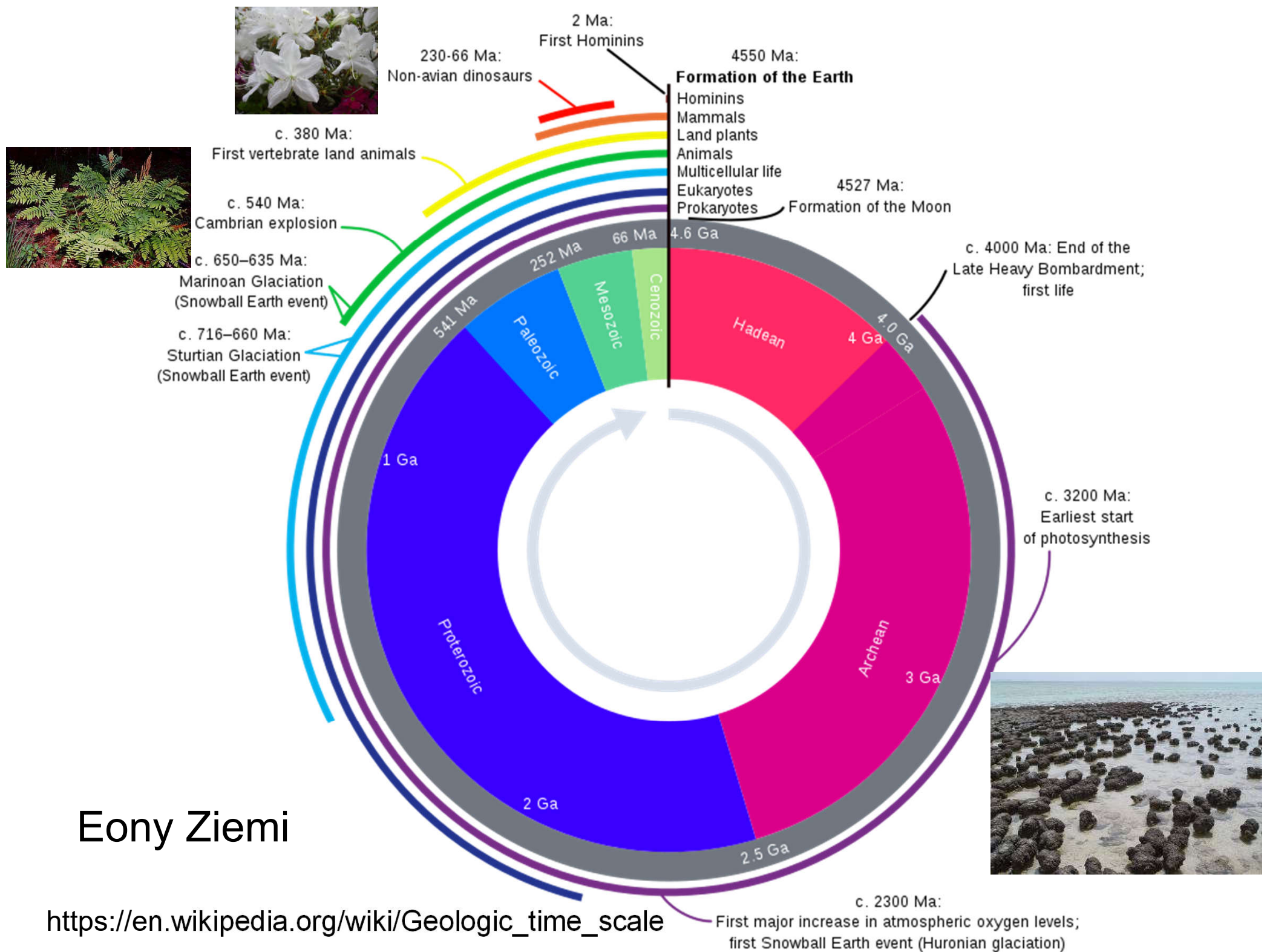
- Chemia fizyczna atmosfery:
- Termodynamika chemiczna i kinetyka w fazie gazowej
- Zasady spektroskopii i fotochemii
- Termodynamika cieczy i roztworów
- Cząstki, aerozole i chmury (fizyczne i chemiczne)
- właściwości, procesy zarodkowania, powstawanie, wzrost...)
- Cykle bio-geo-chemiczne w atmosferze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

«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



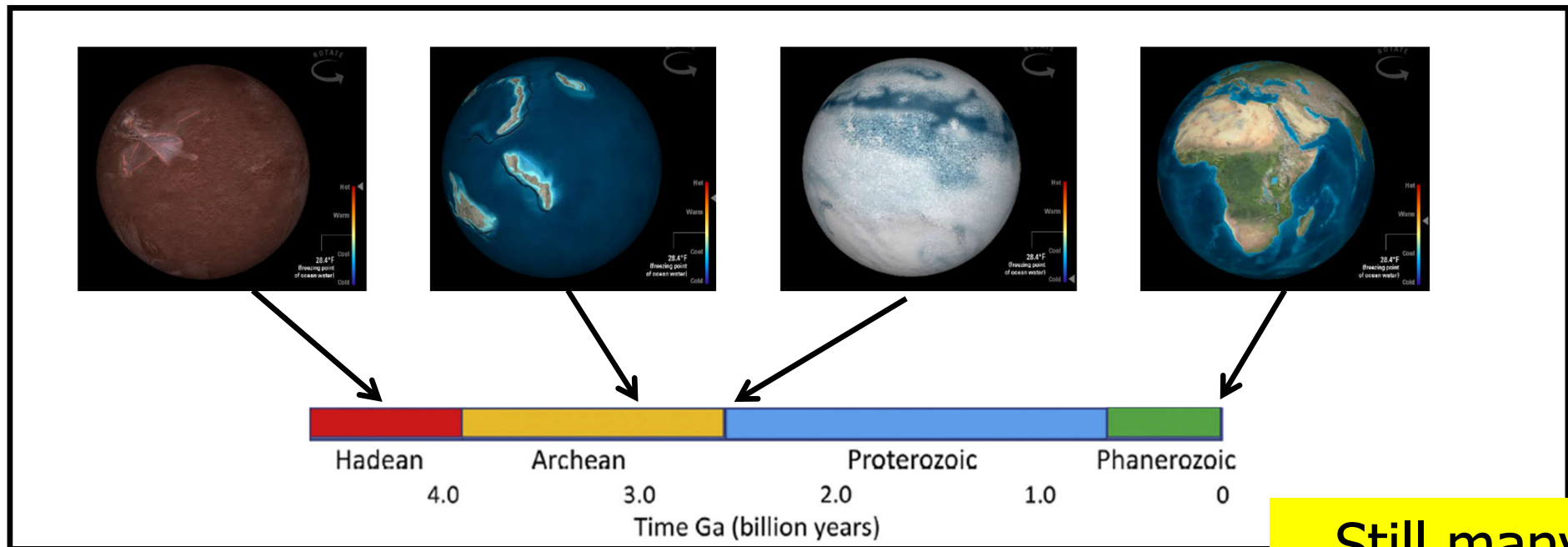
Eony Ziemi

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

Origin and evolution of the Earth's atmosphere

© Daniela Ascenzi, Uni Trento

- 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?



Still many uncertainties

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

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Formation of the Solar system

STEP1: pre-stellar



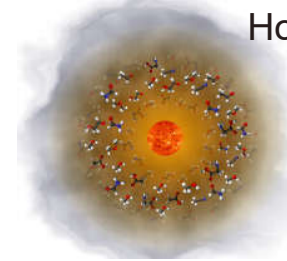
Size $\sim 10^4$ au
Duration $\sim 10^5$ yr
gas+dust $\rightarrow$ icy
mantle formation



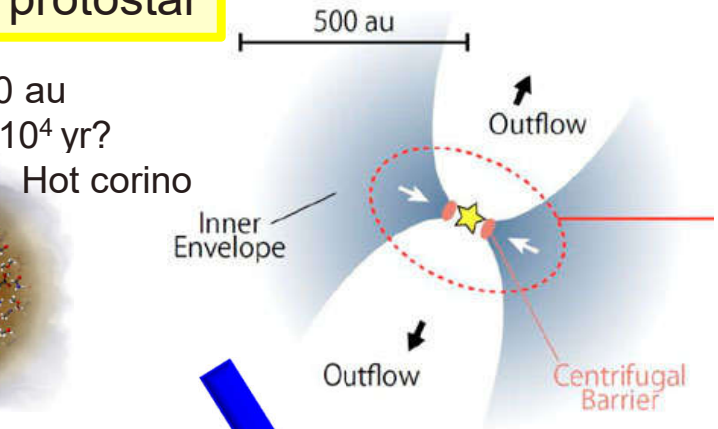
interstellar clouds:
 $\sim 1\%$ dust
 $\sim 99\%$ gas

STEP2: protostar

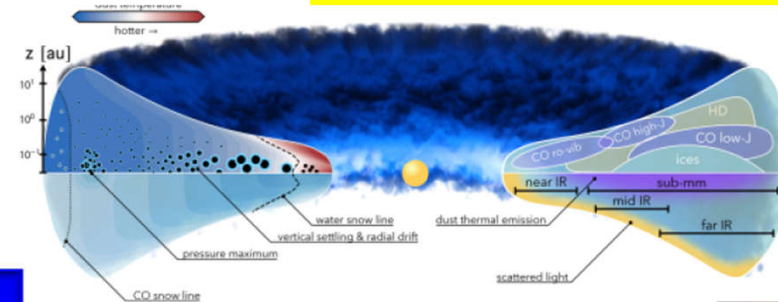
Size $\sim 5-100$ au
Duration $\sim 10^4$ yr?



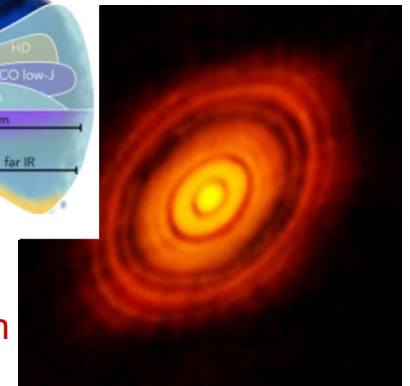
icy mantle
sublimation



STEP3: protoplanetary disk



Size $\sim 10-200$ au
Duration $\sim 10^6$ yr
Dust
agglomeration



STEP4: planetary system

planets
comets
meteorites
asteroids



Small objects
(planetesimals)
accreted or combined
together to build larger
objects (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 occurred in a (cosmologically) very short time – 10 mln years
- About 100 mln years after the beginning of the formation a catastrophic event happened: an 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 billion years cyano-bacteria produced it via photosynthesis from CO_2 , but the initial amount has been buried as iron ores FeO_2 (like on Mars). When iron (in the crust) has been finished, the rest of O_2 went to atmosphere.

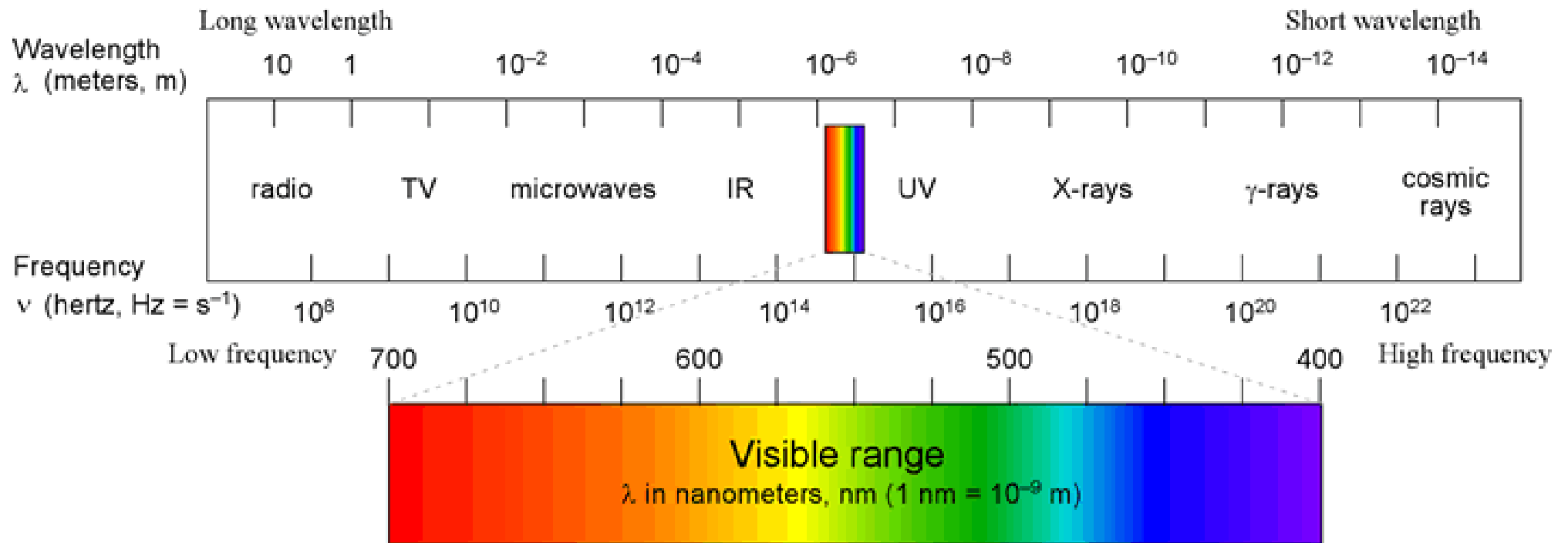
differentiation of the Early earth

<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

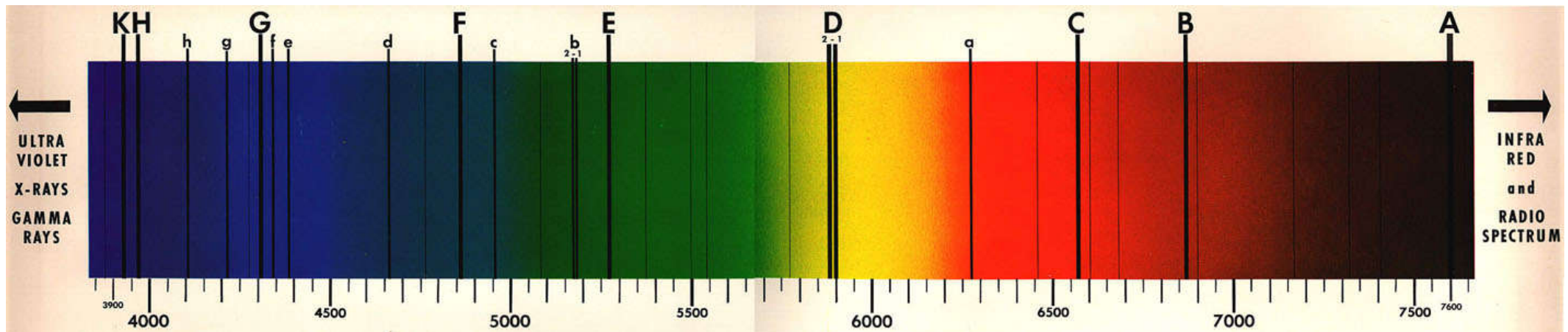
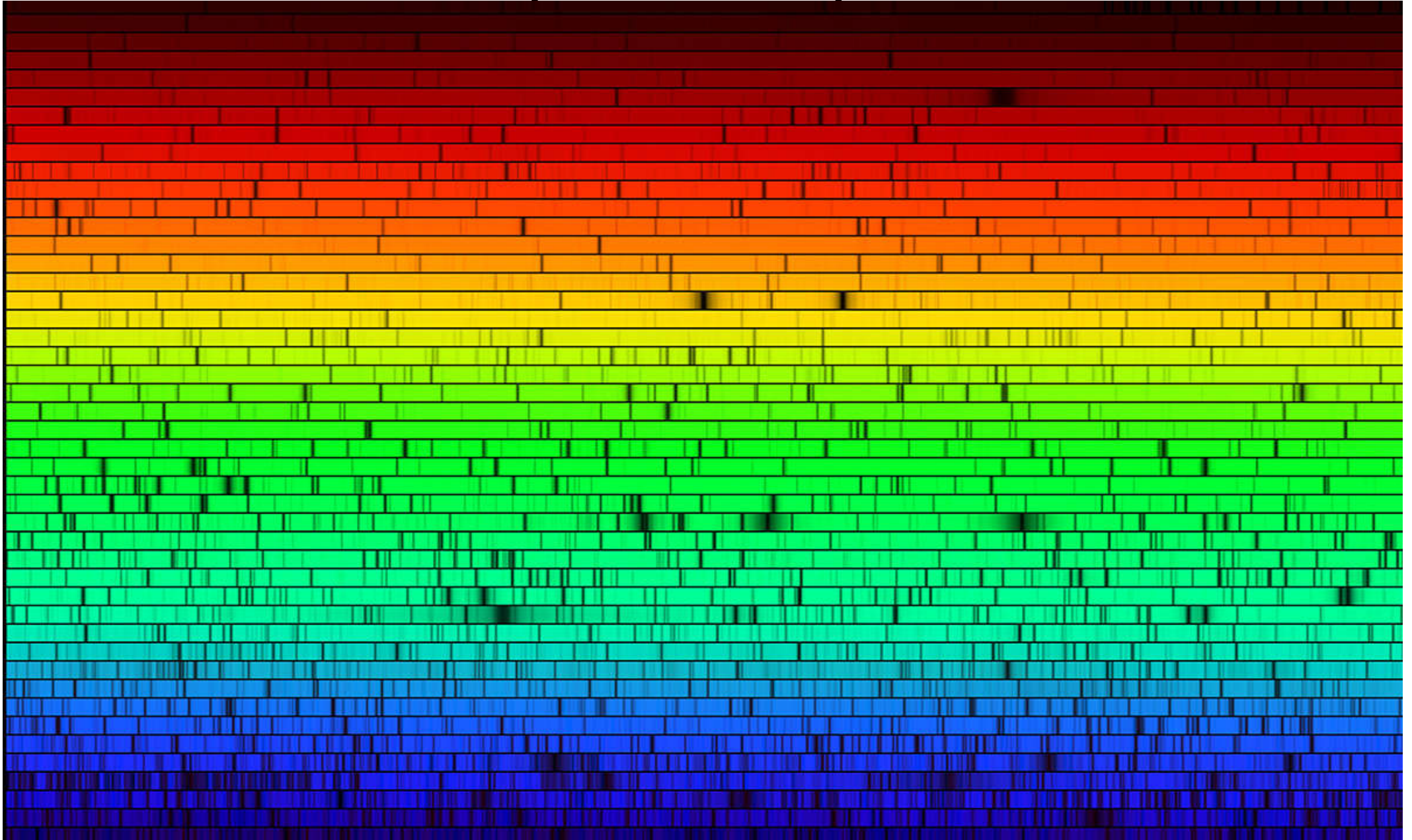


Table 1 -- "Known" Lines		
Designation	Wavelength (Angstrom)	Origin
A	7594	terrestrial oxygen
B	6867	terrestrial oxygen
C	6563	hydrogen (H α)
D ₁	5896	neutral sodium (Na I)
D ₂	5890	neutral sodium (Na I)
E	5270	neutral iron (Fe I)
F	4861	hydrogen (H β)
H	3968	ionized calcium (Ca II)
K	3934	ionized calcium (Ca II)

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	Tlen	O ₂	20,95	
3	Argon	Ar	0,93	
4	Dwutlenek węgla	CO ₂	od 0 do 0,033	
Składniki drugorzędne				
	Niezmienne		koncentracja	trwale
5	Neon	Ne	18 ppm	
6	Hel	He	5 ppm	
7	Krypton	Kr	1 ppm	
8	Ksenon	Xe	0,09 ppm	
9	Metan	CH ₄	1,5 ppm	półtrwale
10	Tlenek węgla	CO	0,1 ppm	
11	Wodór	H ₂	0,5 ppm	
12	Podtlenek azotu	N ₂ O	0,25 ppm	
				2 · 10 ⁷ lat
				5 ÷ 10 lat
				3 · 10 ⁶ lat
				3 lata
				0,35 lat
				< 200 lat

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 ₂ S	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 ₂ O	0 ÷ 10 ppb		

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 ₂ O	0.31 ppmv	150 years

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:

$CF_2Cl_2 + h\nu \rightarrow CF_2Cl + Cl$ (photolysis of CFCs in the stratosphere)

$HONO + h\nu \rightarrow OH + NO$ (source of OH in the troposphere)

$NO_2 + h\nu \rightarrow O + NO$ (source of O_3 in the troposphere)

$NO_3 + h\nu \rightarrow O_2 + NO$ or $O + NO_2$ (removal of NO_3 generated at night)

$Cl_2 + h\nu \rightarrow Cl + Cl$ (source of Cl atoms)

$H_2CO + h\nu \rightarrow H_2 + CO$ 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

- greenhouse 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 ($\lambda=100\text{-}800\text{ nm}$)

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

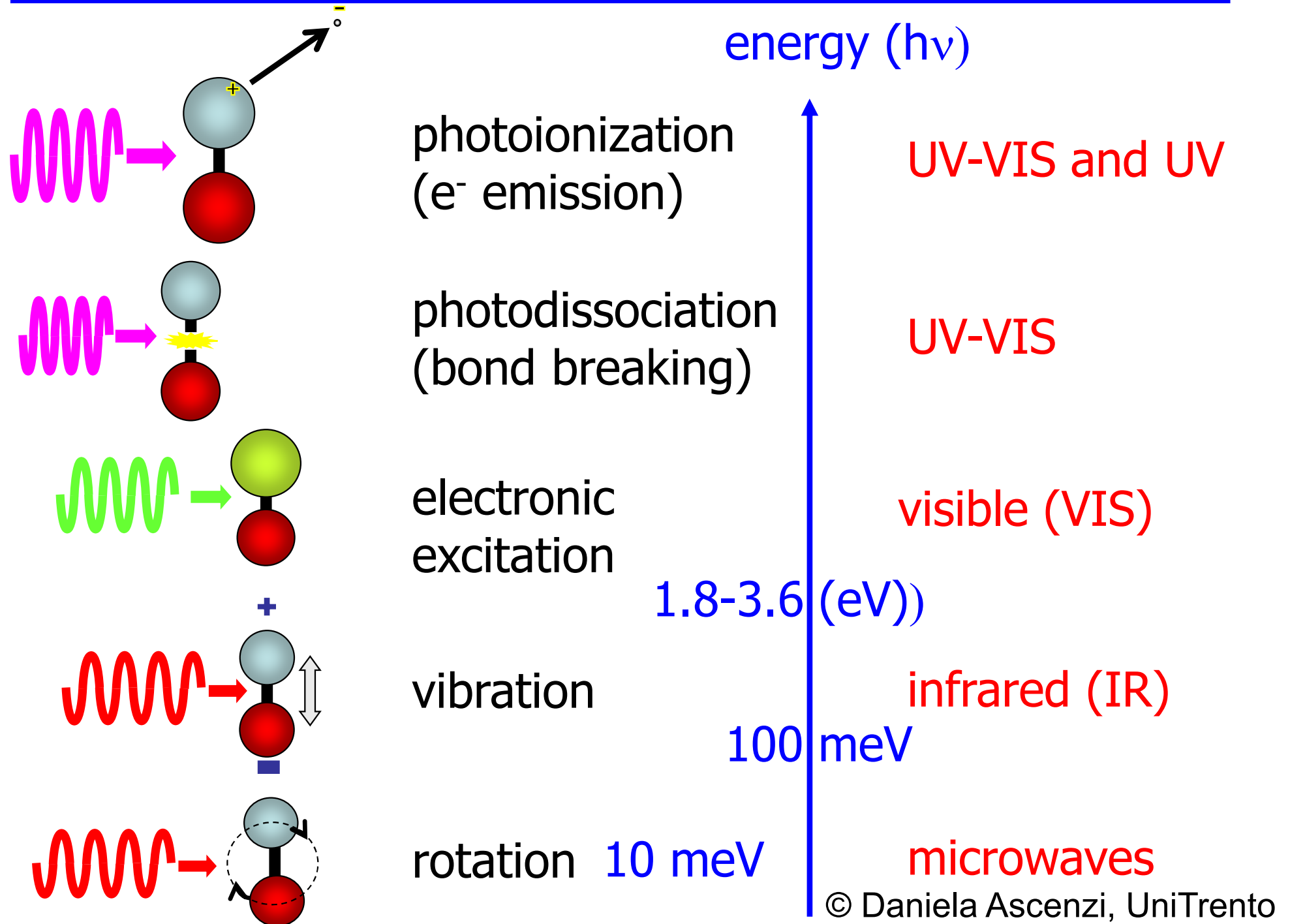
IR radiation ($\lambda=0.8 - 300\text{ }\mu\text{m}$)

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

MW radiation ($\lambda = 0.5 - 300\text{ mm}$)

- excites rotational motions in molecules

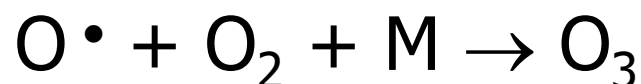
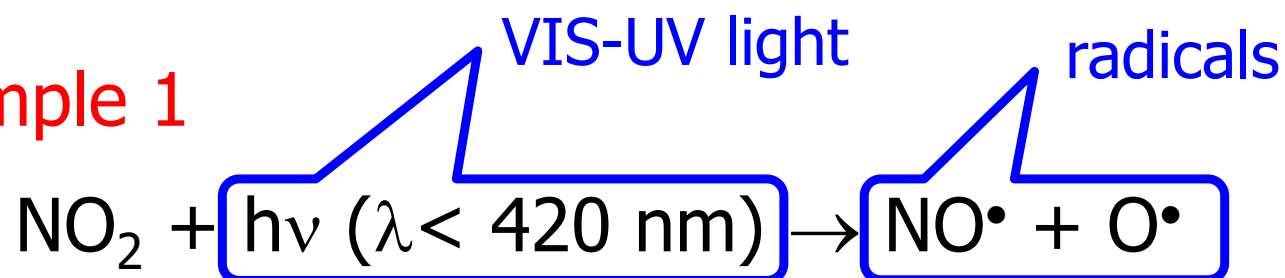
Photophysical and chemical processes



Photochemical processes

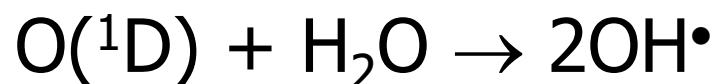
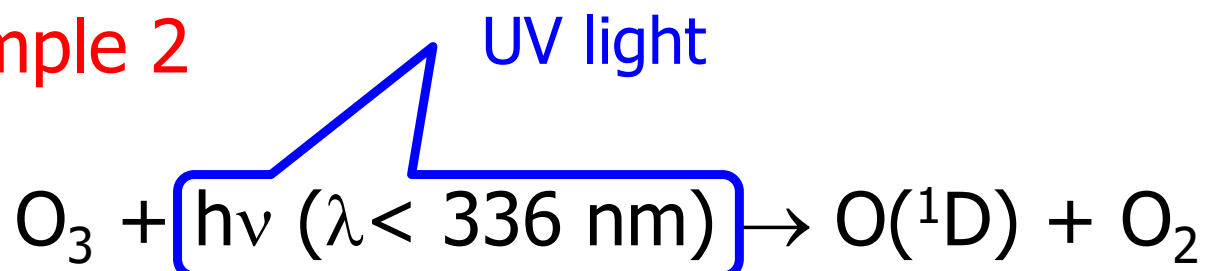
Several important chemical processes in the atmosphere are initiated by light absorption

Example 1



photochemical smog

Example 2



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

Photon energies and bond dissociation energies

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

This energy is sufficient to break:

- weak chemical bonds (e.g. $\text{O}_2\text{-O}$ in ozone $\sim 100 \text{ kJ/mol}$)



- moderately strong C-H bonds (e.g. formaldehyde $\sim 368 \text{ kJ/mol}$)

Związki o znaczeniu chemicznym

Tablica 3.6

Związki o dużym znaczeniu dla chemii atmosfery

związki siarki	związki azotu	związki węgla	inne
H_2S SO_2 $\text{SO}_3, \text{SO}_4^{2-}$ utlenianie	$\text{NH}_3, \text{NH}_4^+$ N_2O NO NO_2 NO_3^-	CH_4 CO CO_2	H_2 O_3
R	R B NZ R R	B NZ B NZ NZ	B NZ

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, N₂O, and NO₂

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



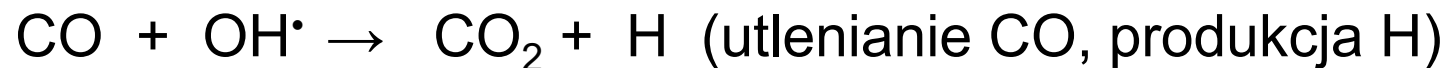
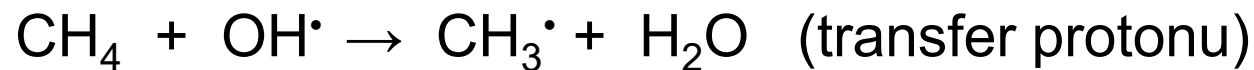
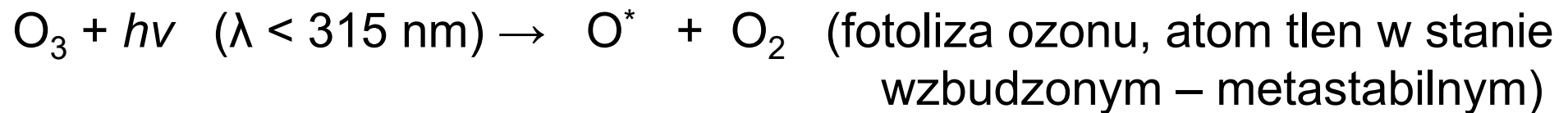
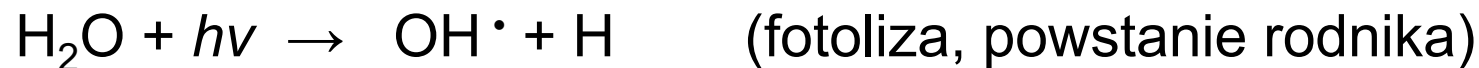
+ Author & Article Information

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

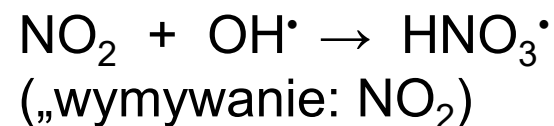
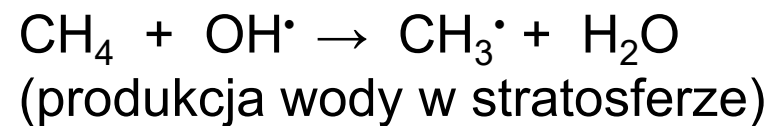
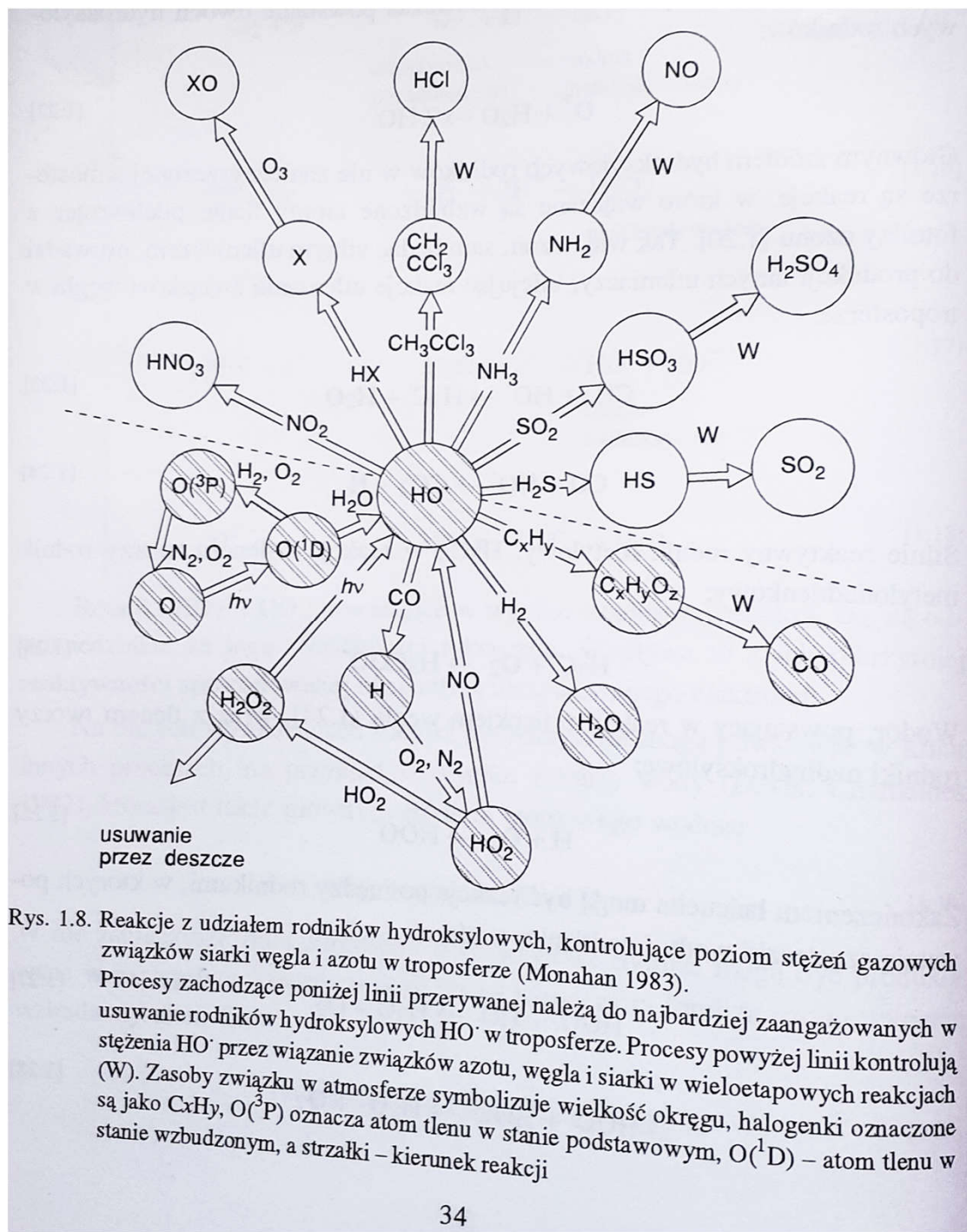
<https://doi.org/10.1063/1.5114722> Article history 

Reakcje chemiczne: cząsteczki, jony, rodniki

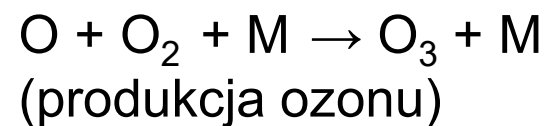
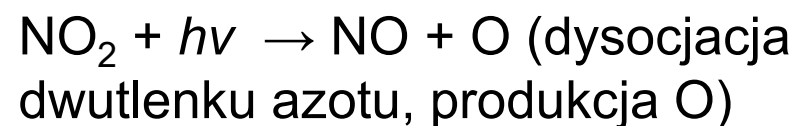
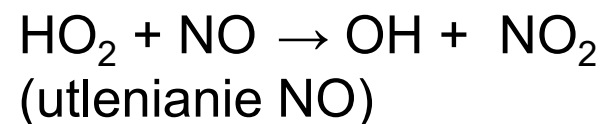
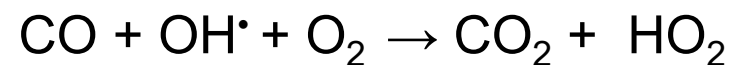
Rodnik – atom, cząsteczka, fragment cząsteczki z *niesparowanym* elektronem: stąd ogromna reaktywność rodników



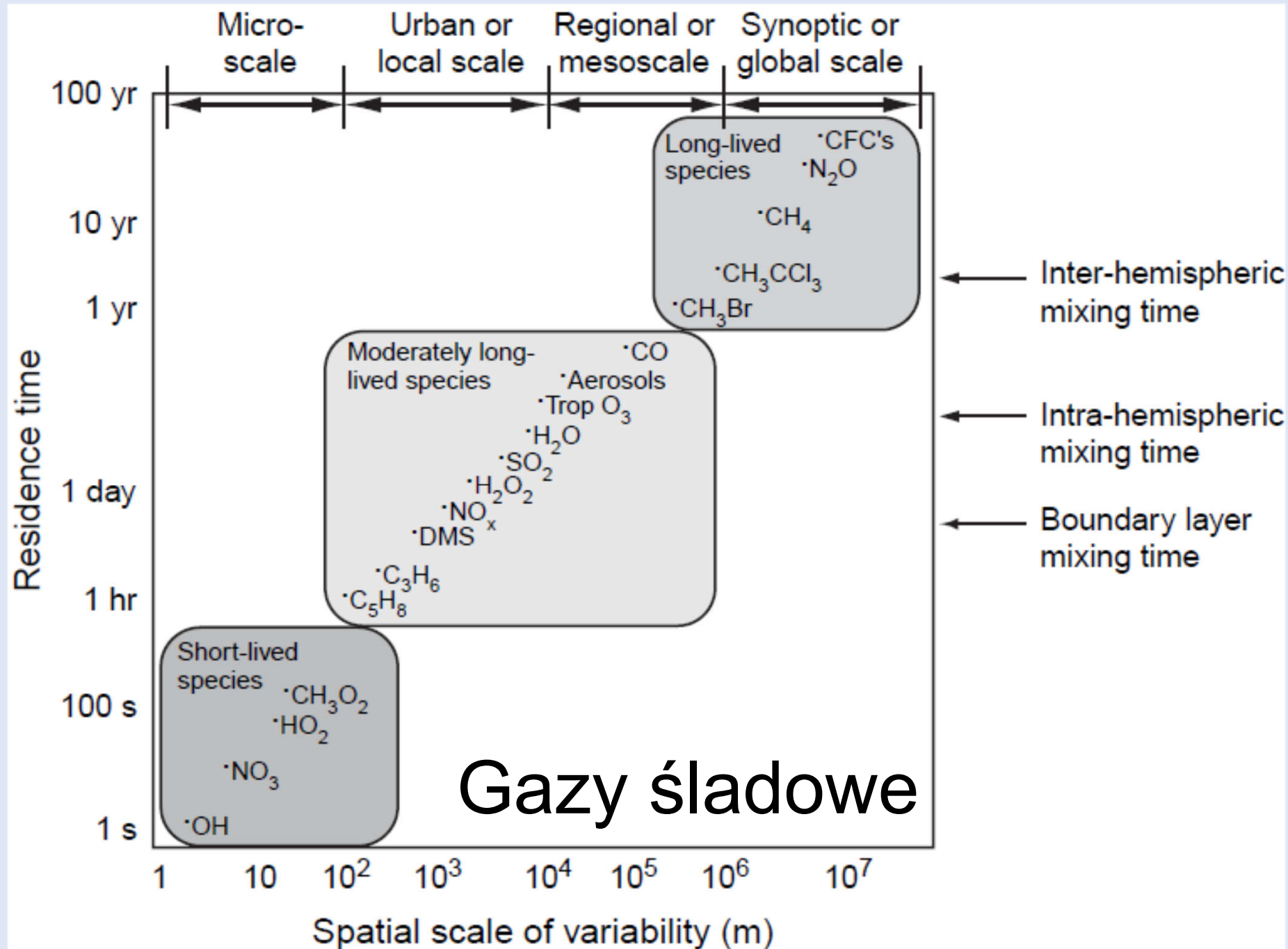
Rodnik hydroksylowy – detergent (oczyszczacz) atmosfery



I cały łańcuch reakcji:



(*Atmospheric Science*, srt. 167)



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



G. Karwasz. IAEA Meeting, Vienna, 23.11.2019



„Recommended” cross sections for electron scattering with molecules

Mi-Young Song, Jung-Sik Yoon,

Plasma Technology Research Center, National Fusion Research Institute, Gunsan, South Korea

Hyuck Cho

Department of Physics, Chungnam National University, Daejeon, South Korea

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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.

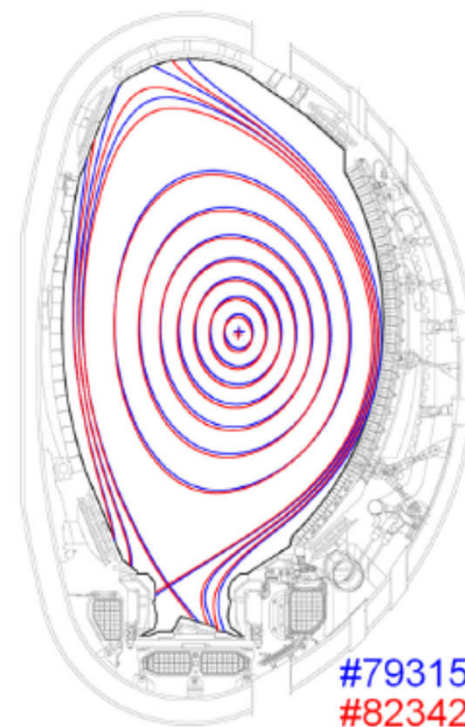


Figure 1. Magnetic equilibria for the shots #79315 and #82342 at 20 s and 13 s, respectively.

Data needed:

I Neutrals (H, C, C₂, Be, BeH₂, CH₄)

1. Total cross section

2. Partial cross sections:

elastic scattering $e+A \rightarrow e+A$ (from 0 eV)

rotational excitation $e+\text{CH}_4 (J=0) \rightarrow e+\text{CH}_4 (J=2)$ i.e. 5 meV

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

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

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

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

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

emission from dissociation $e + \text{AB} \rightarrow \text{A}^* + \text{B} + e + h\nu$

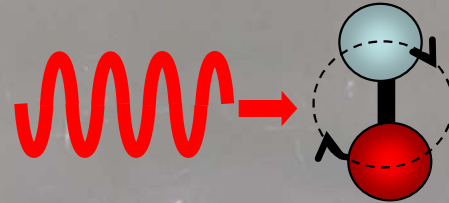
ionization $e+A \rightarrow \text{A}^+ + 2e$ 10 eV

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

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

Energy levels

rotation
microwaves

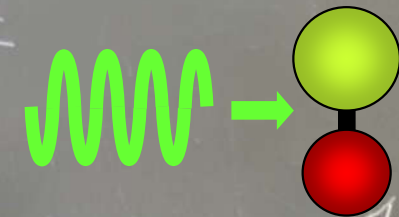
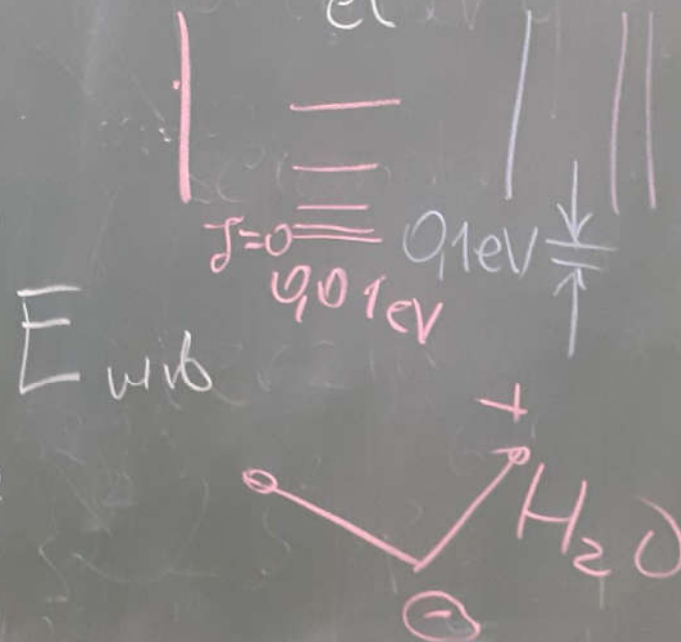
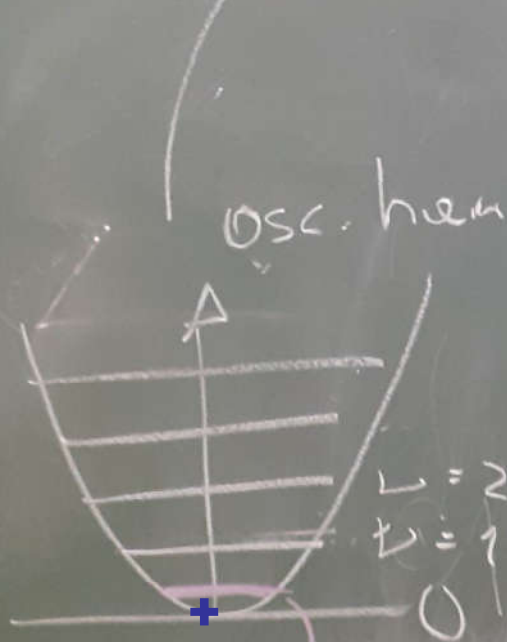


electronic
excitation

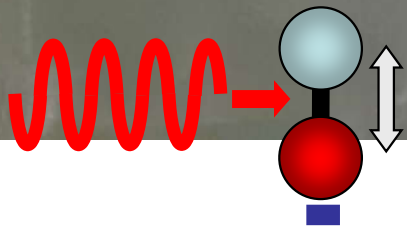
visible (VIS)

$$E_{\text{rot}} = B J(J+1)$$

$$E_{\text{el}} = R \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$



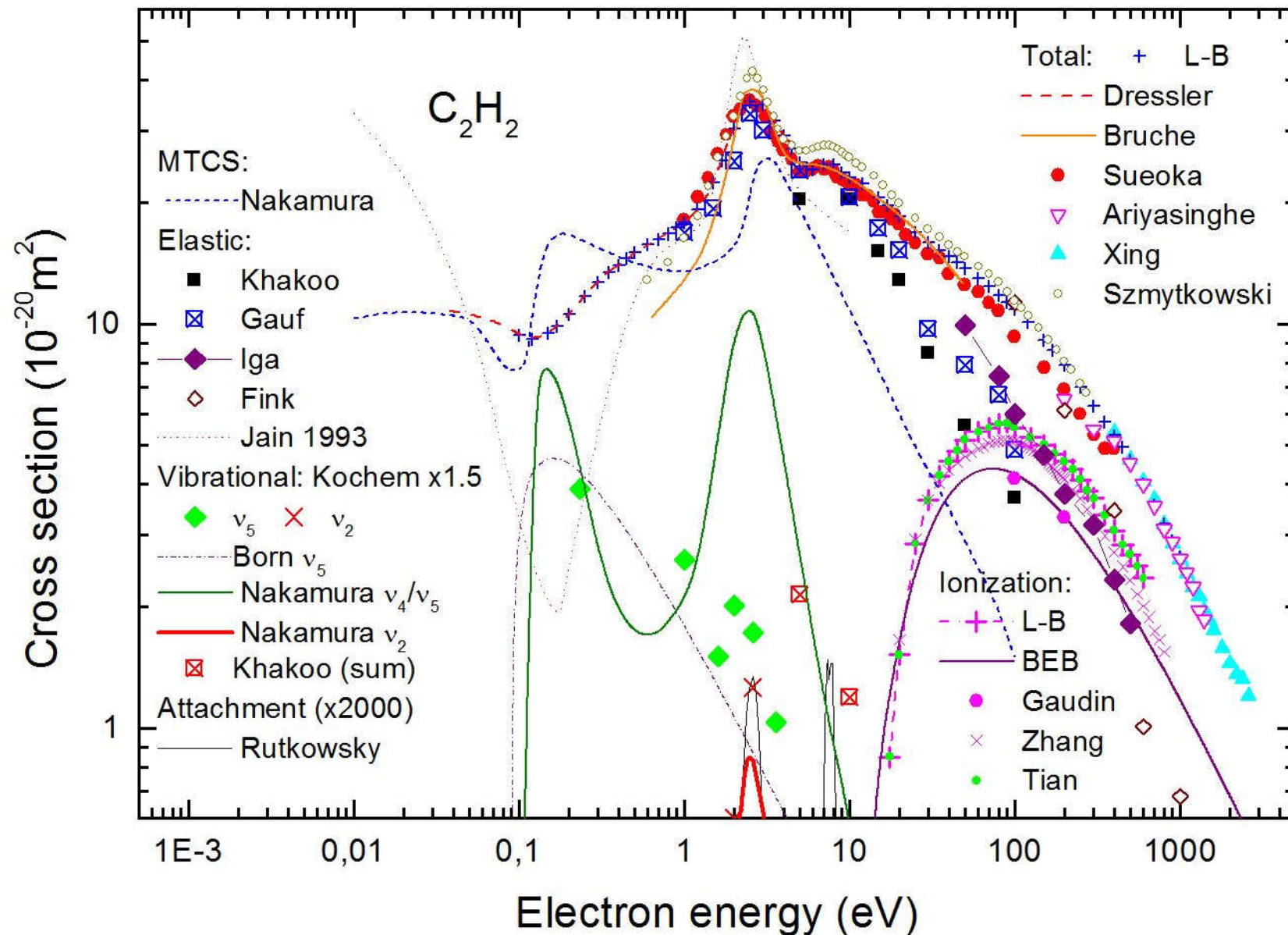
$$1.8 \text{ eV} - 760 \text{ nm}$$



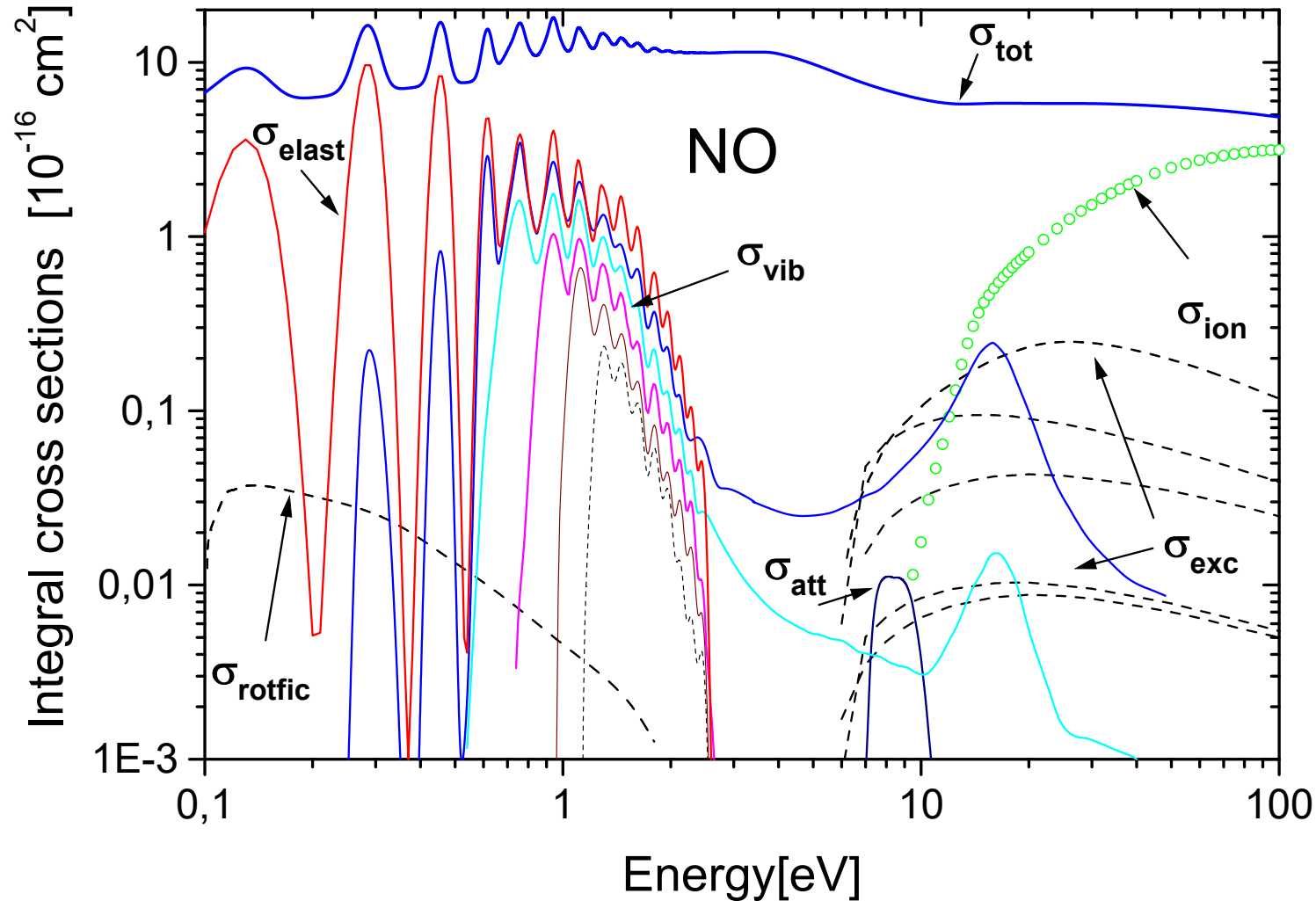
infrared (IR)

vibration

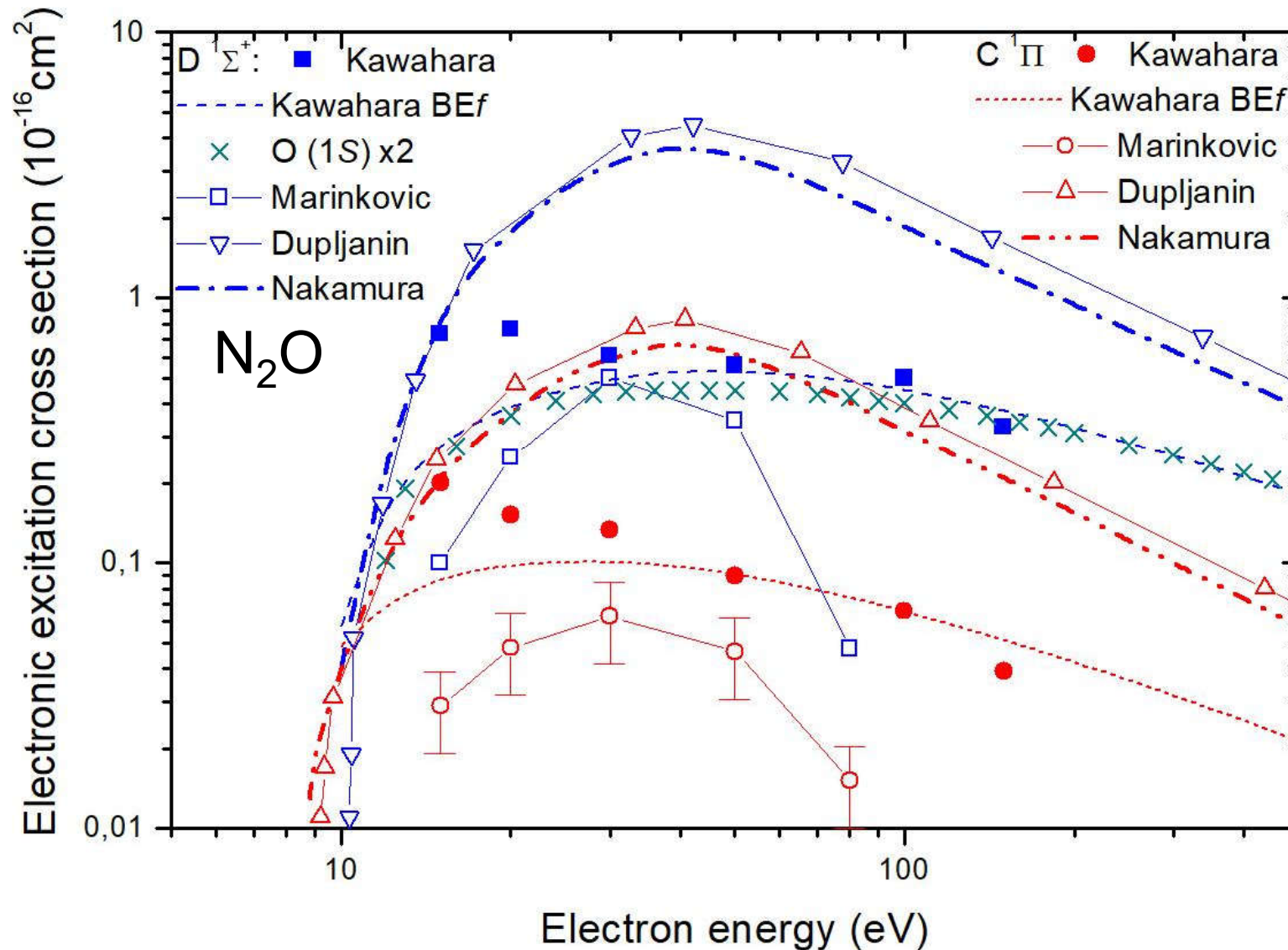
Total & partial cross sections: C₂H₂



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

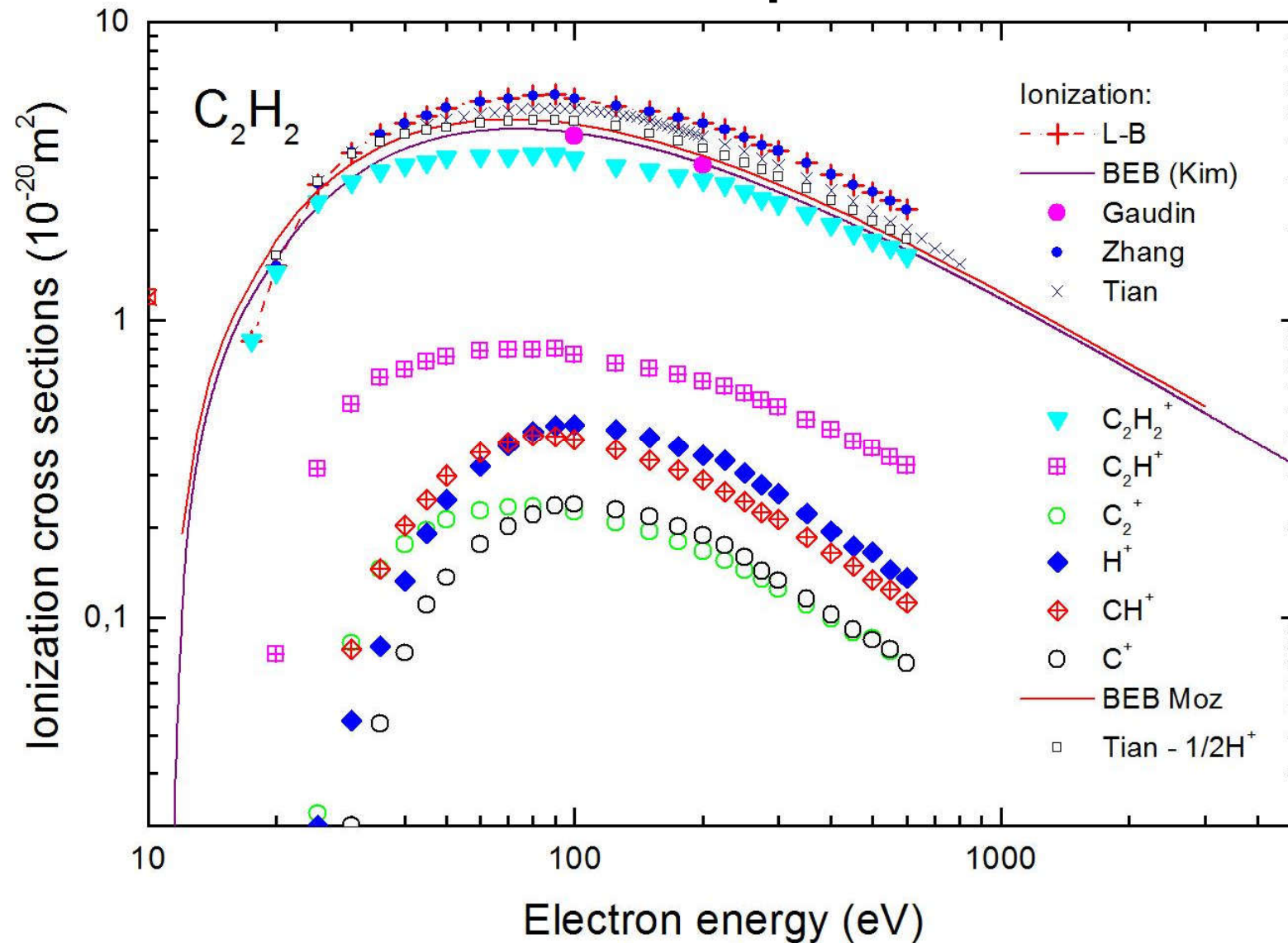


Electronic excitation: optically allowed and forbidden states



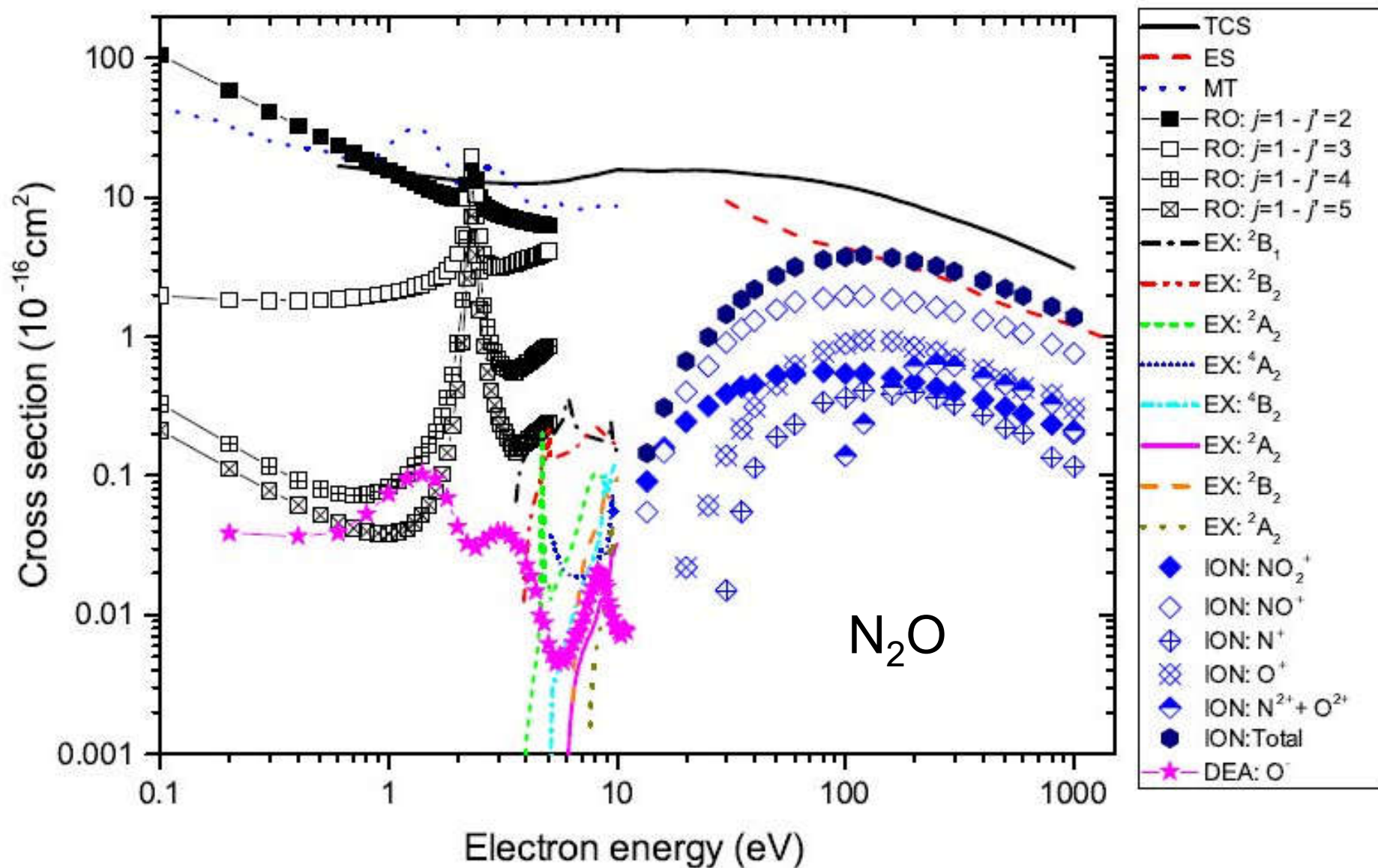
Electronic excitation is relatively small part of total (or ionization) cross section

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)

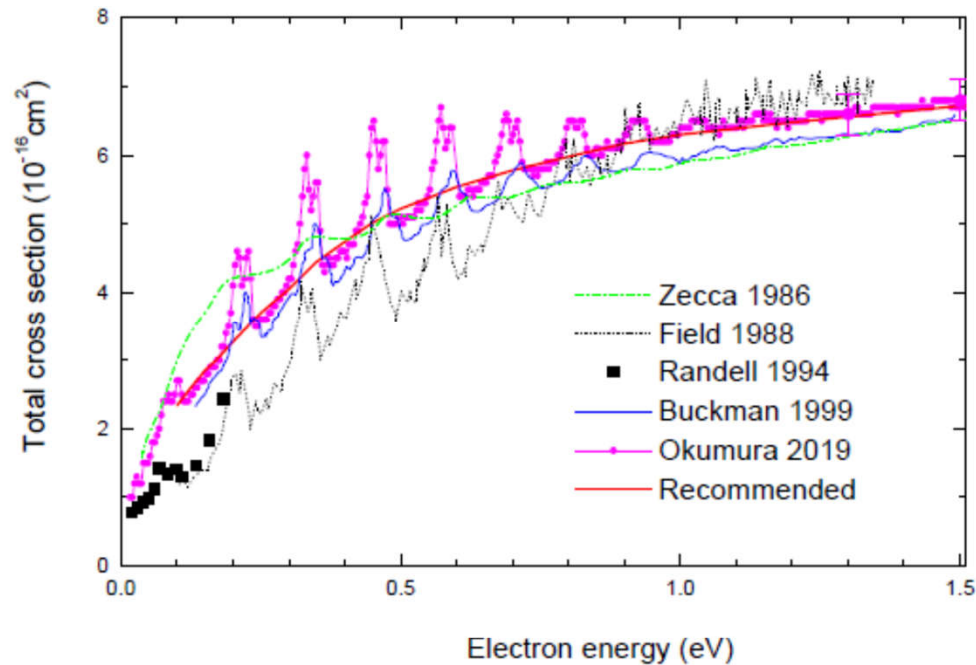


FIG. 2. Experimental total cross sections for electron scattering from O₂ in the very-low energy range: green dash-dot line,

Very-low energy resonant scattering

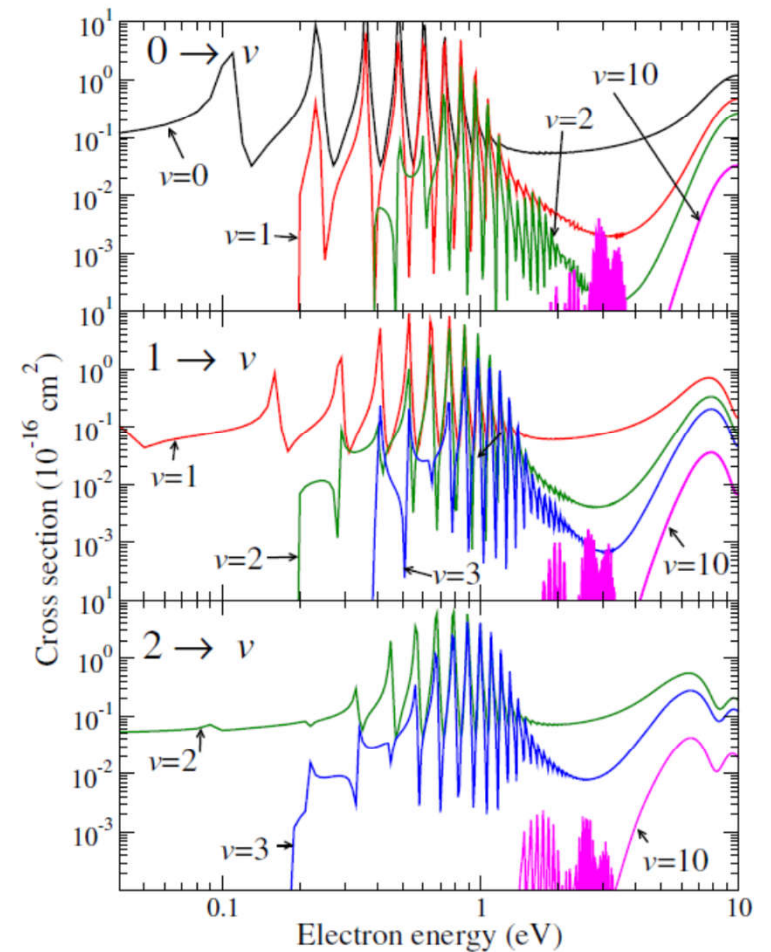


FIG. 7. Examples of the recommended cross sections for vibrational excitation for several transition obtained by La-

Electronic excitations and transitions between states

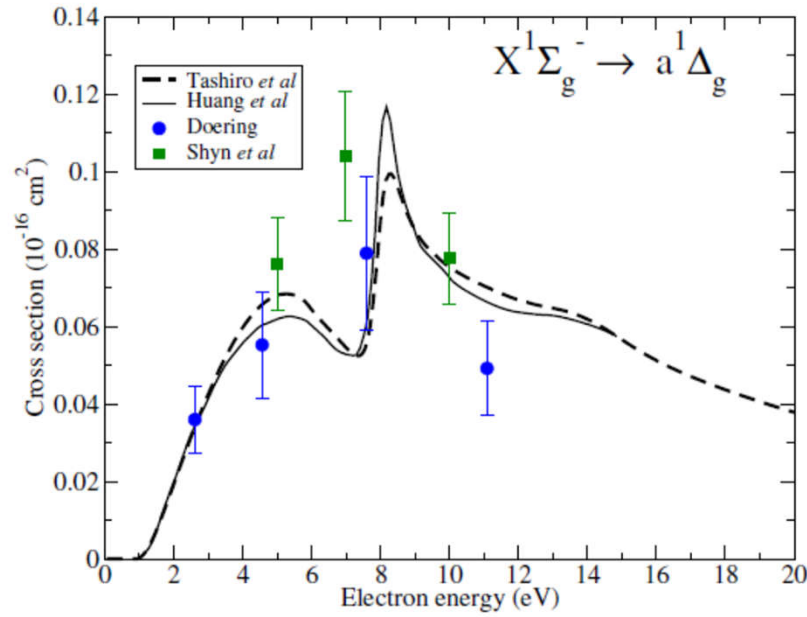


FIG. 8. Electronic excitation cross section for the $X^1\Sigma_g^- \rightarrow a^1\Delta_g$ transition. The solid line - Huang, Zhang,

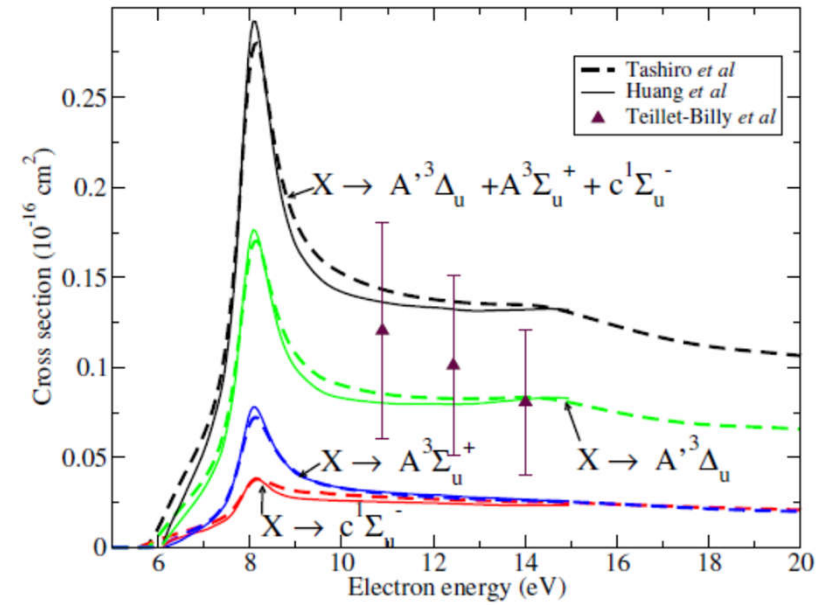


FIG. 10. Electronic excitation cross section for the $X^3\Sigma_g^- \rightarrow c^1\Sigma_u^-$ (red lines), $X^3\Sigma_g^- \rightarrow A^3\Sigma_u^+$ (blue lines), and

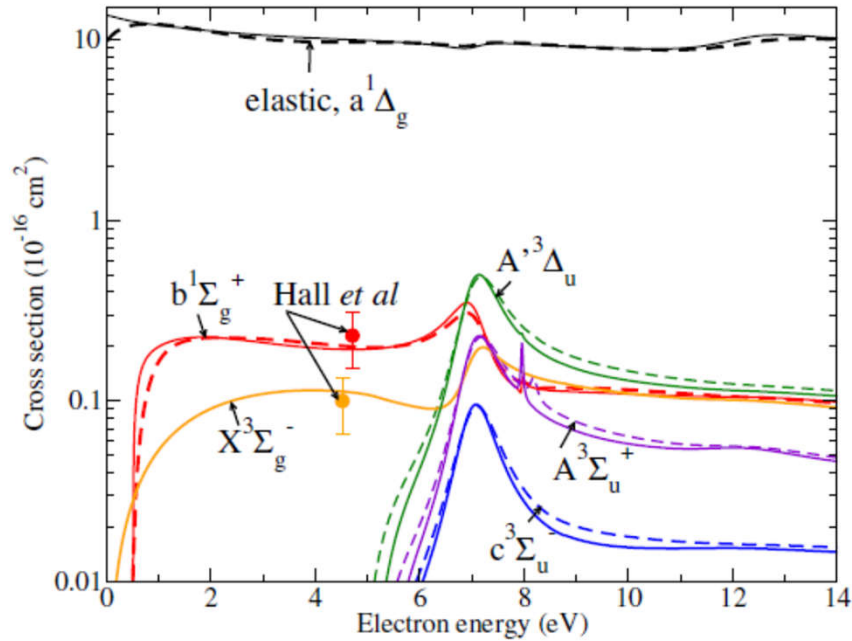


FIG. 11. Cross sections for elastic and inelastic transi-

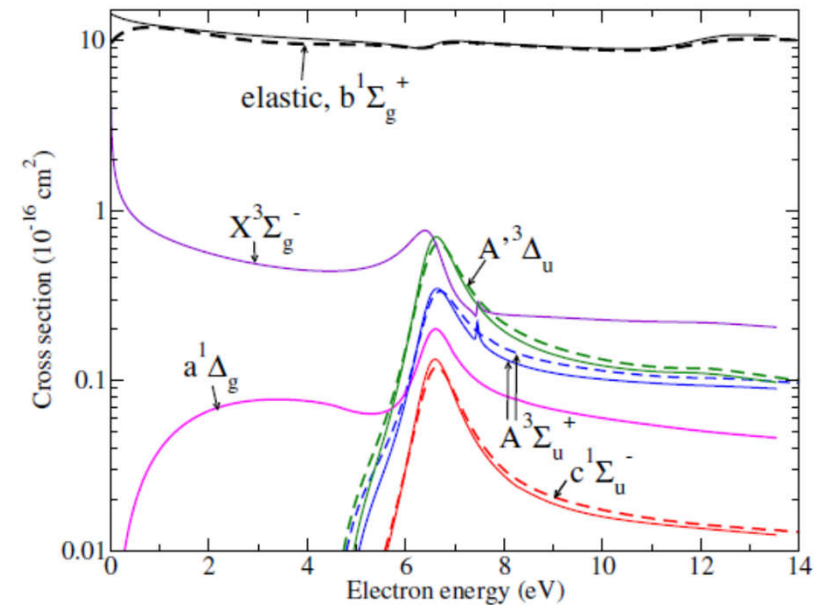


FIG. 12. Similar to Fig. 11 for the elastic and inelastic transitions starting from the metastable $b^1\Sigma_g^+$ state. The cross sections are taken from Ref. 71.

Titan's atmosphere

CRITICAL REVIEW OF N, N⁺, N₂⁺, N⁺⁺, And N₂⁺⁺ MAIN PRODUCTION PROCESSES AND REACTIONS OF RELEVANCE TO TITAN'S ATMOSPHERE

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PASCAL PERNOT⁴, NADIA BALUCANI⁵, PIERGIORGIO CASAVECCHIA⁵, ANDRÉ CANOSA⁶, SÉBASTIEN LE PICARD⁶,
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ABSTRACT

This paper is a detailed critical review of the production processes and reactions of N, N⁺, N₂⁺, N⁺⁺, and N₂⁺⁺ 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 N₂ (A ³Σ_u⁺), N (⁴S), N (²D), N (²P), N₂⁺, N⁺ (³P), N⁺ (¹D), N₂⁺⁺, and N⁺⁺ species, and includes a critical survey of the reactions of N, N⁺, N₂⁺, N⁺⁺, and N₂⁺⁺ with N₂, H₂, D₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₈ and the deuterated hydrocarbon analogs, as well as the recombination reactions of N₂⁺, N⁺, N₂⁺⁺, and N⁺⁺. Production processes, lifetimes, and quenching by

Table 1

Dissociation and Ionization Thresholds of N₂, as well as Lifetimes of Excited States

	Species	Threshold Energy (eV)	Remarks
	N ₂ (X ¹ Σ _g ⁺)	0	
1)	N ₂ (A ³ Σ _u ⁺)	6.22	N ₂ (A) lifetime = 2.37 s (a)
	N (⁴ S) + N (⁴ S)	9.76	Not observed
2)	N (² D) + N (⁴ S)	12.14	N (² D) lifetime = 13.6 hr and 36.7 hr * (b)
	N (² P) + N (⁴ S)	13.33	N (² P) lifetime = 11.1 s and 10.5 s ** (b)
	N (² D) + N (² D)	14.52	
3)	N ₂ ⁺ (X ² Σ _g ⁺)	15.58	
	N ₂ ⁺ (A ² Π _u)	16.93	N ₂ ⁺ (A) lifetime = 13.9 – 7.3 ms *** (c)
	N ₂ ⁺ (B ² Σ _u ⁺)	18.75	N ₂ ⁺ (B) lifetime = 67 ns (d)
4)	N ⁺ (³ P) + N (⁴ S)	24.29	
	N ⁺ (¹ D) + N (⁴ S)	26.19	N ⁺ (¹ D) lifetime = 258 s (e)
	N ⁺ (³ P) + N (² D)	26.68	
	N ⁺ (³ P) + N (² P)	27.87	Not observed
	N ⁺ (¹ S) + N (⁴ S)	28.35	Not observed
	N ₂ ⁺⁺ (X ¹ Σ _g ⁺)	42.88	N ₂ ⁺⁺ lifetime = 3 s (f)
	N ⁺ (³ P) + N ⁺ (³ P)	44.5	
	N ⁺⁺ (² P) + N (⁴ S)	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
N₂ is one of the most stable molecules
- 3) Ionization threshold 15.6 eV (much higher than H atom)
- 4) Ionization threshold for N₂⁺ (N₂⁺ → N₂⁺⁺ + e⁻) = 24.29 eV (metastable)

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

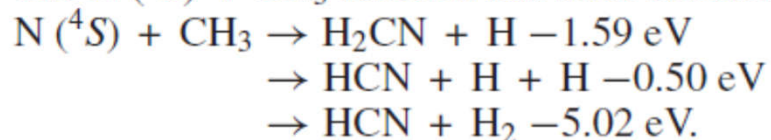
Reaction	T (K)	k ($\text{cm}^3 \text{s}^{-1}$)	Method	Reference
$N_2 (A^3\Sigma_u^+) + N_2$	298	$\leq 10 \times 10^{-18}$	FP-CL	(Callear & Wood 1971)
$N_2 (A^3\Sigma_u^+) + N_2$	298	$\leq 3.7 \times 10^{-16}$	PR-RA	(Dreyer & Perner 1973)
$N_2 (A^3\Sigma_u^+) + N_2$	298	4.5×10^{-17}	DF	(Vidaud et al.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

Reaction	T (K)	k ($\text{cm}^3 \text{s}^{-1}$)	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	$\leq 6 \times 10^{-15}$	FP-CL	(Black et al. 1969)
$N (^2D) + N_2$	298	1.6×10^{-14}	DF-RA	(Lin & Kaufman 1971)

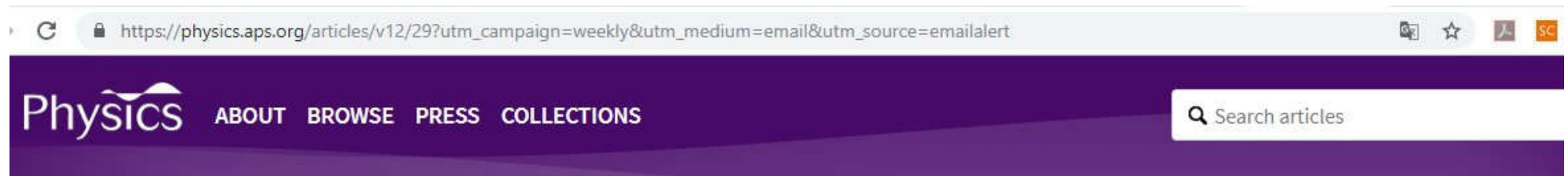
Products:

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

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



Thunderstorm: electric discharge 1,3 GV



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.



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

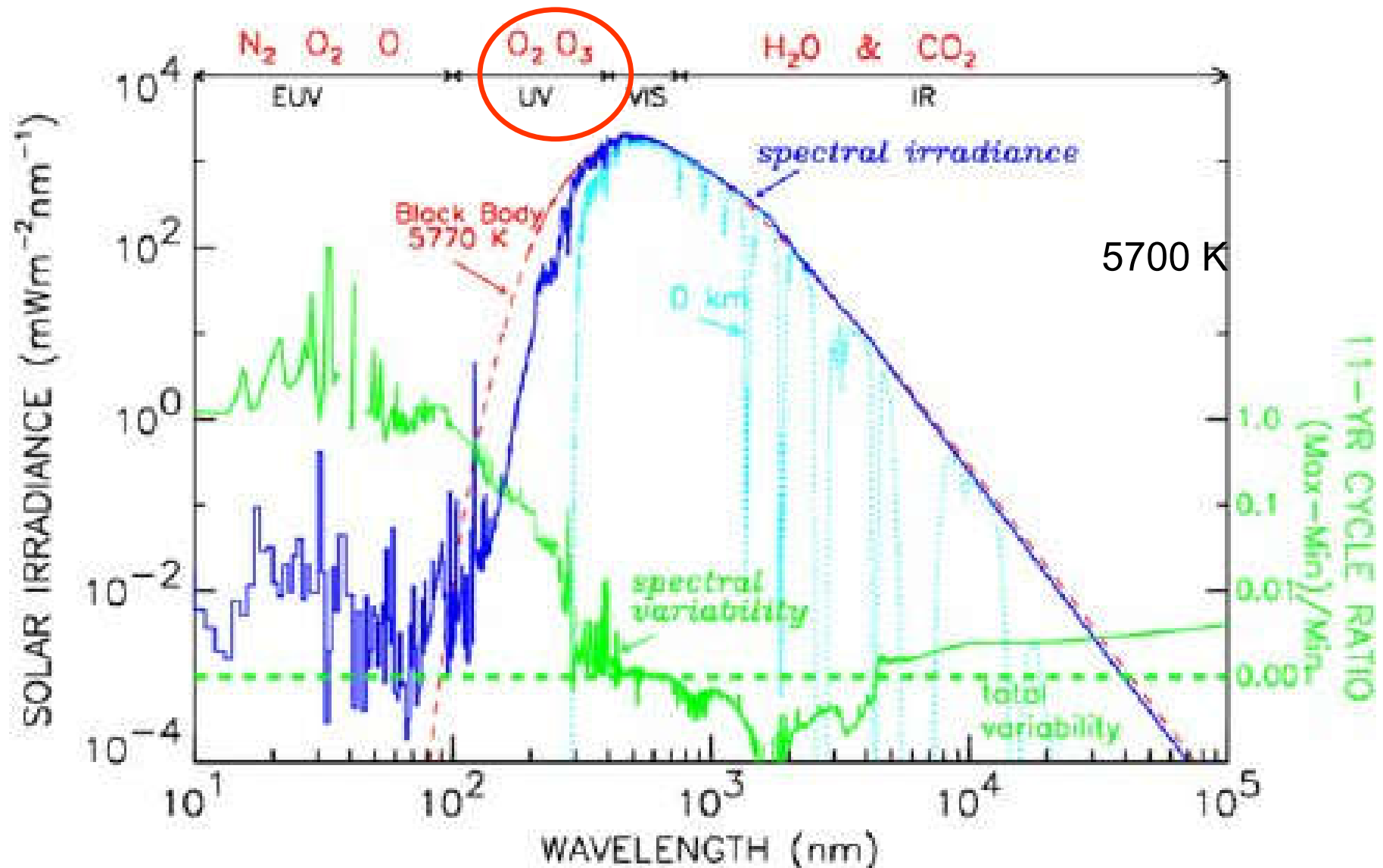
Features

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.

Widmo Słońca, poza atmosferą

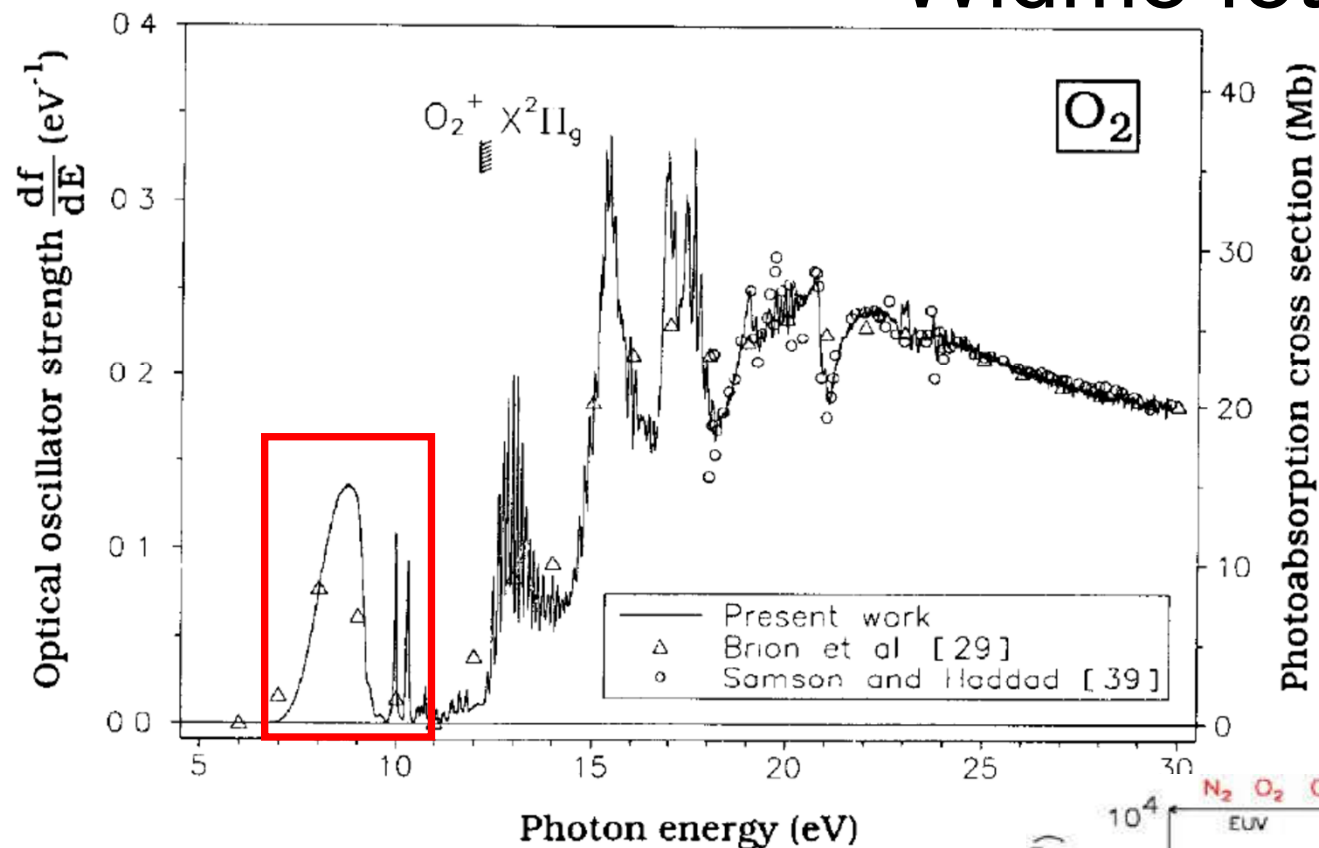


Wiosną jest znacznie więcej UV niż jesienią: latem powstaje ozon

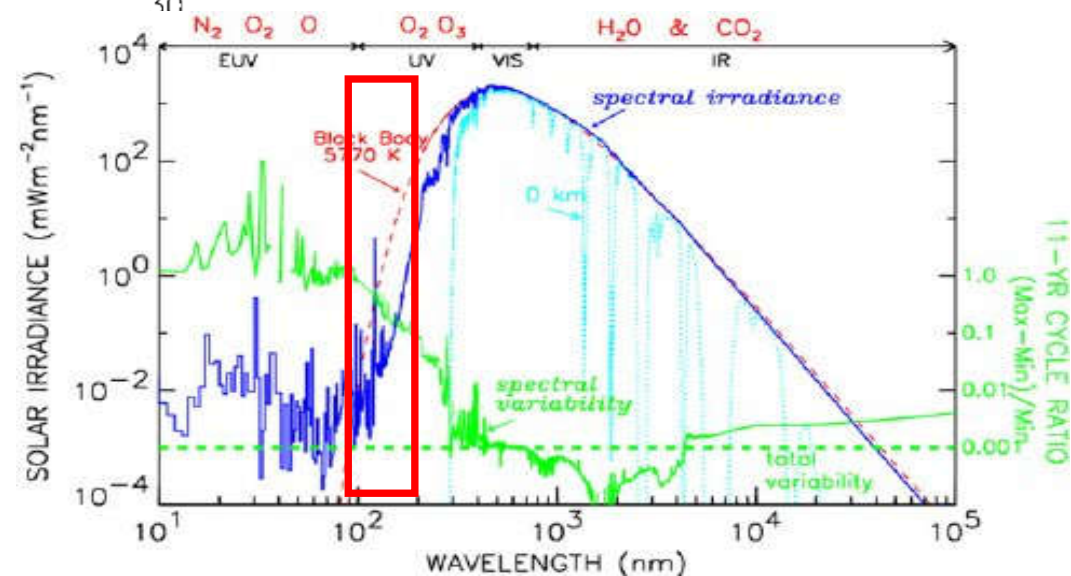
Asta Juzeniene et al. , Solar radiation and human health

• [Reports on Progress in Physics](#) 74(6):066701.May 2011, DOI: [10.1088/0034-4885/74/6/066701](https://doi.org/10.1088/0034-4885/74/6/066701)

Widmo fotoabsorpcji O₂

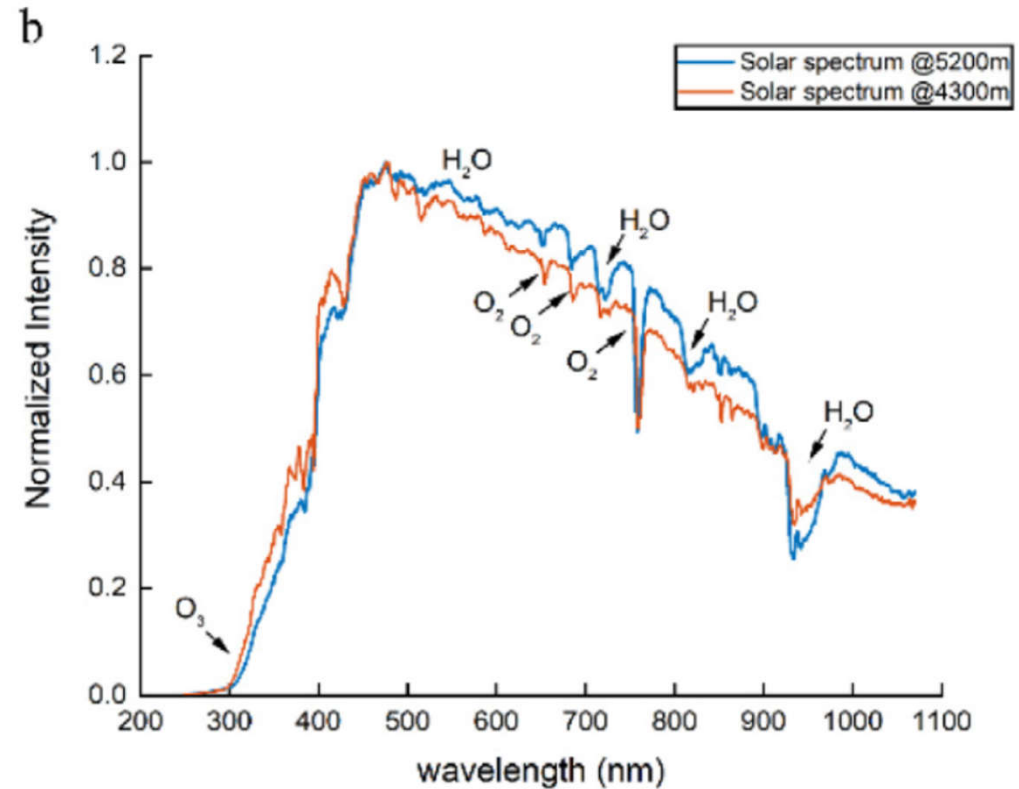
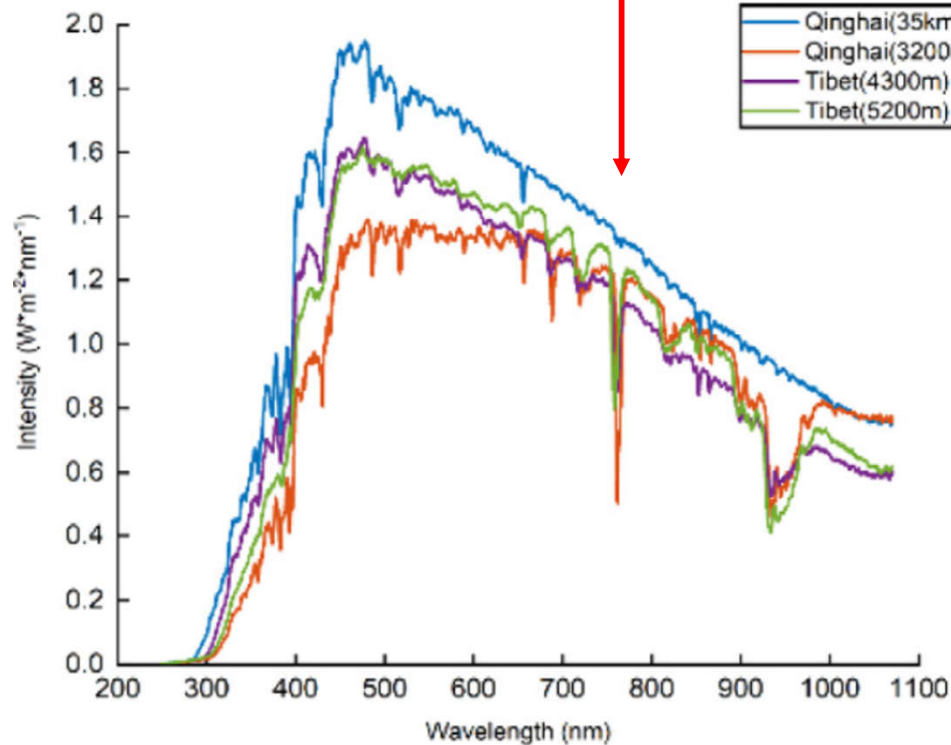


6.5 - 12 eV
tj. c.a. 100 – 200 nm



Absorpcja optyczna tlenu (O_2)

O_2 $b^1\Sigma_g$ metastable state

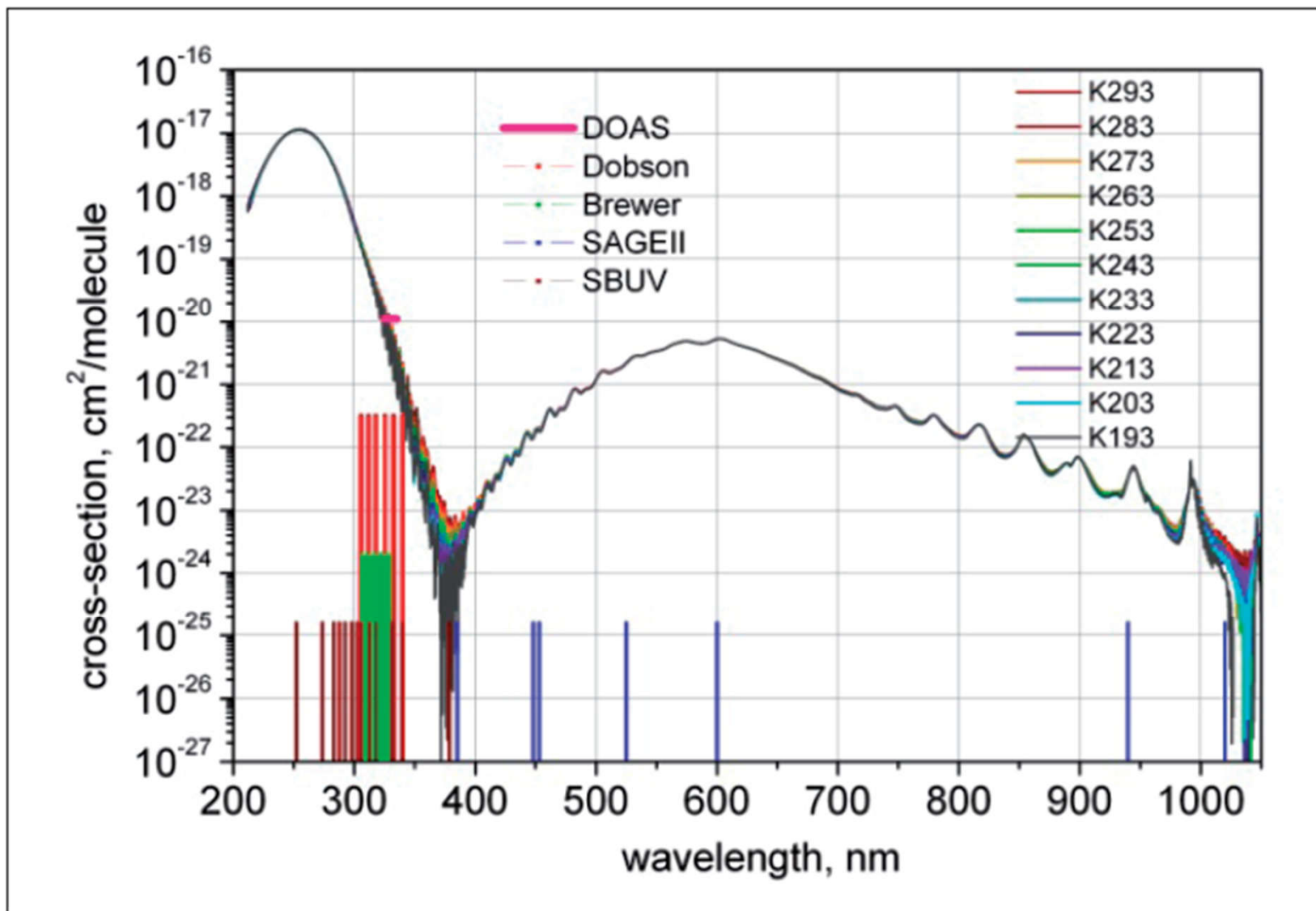


Tlen cząsteczkowy – tylko w troposferze,
na wysokości 35 km – brak absorpcji linii 760 nm

Xu i in., 2023, <https://doi.org/10.1016/j.egy.2023.04.229>

Pomiary za pomocą balonu stratosferycznego

Widmo absorpcji UV, VIS i IR ozonu O₃



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

Rodnik („detergent”) OH-

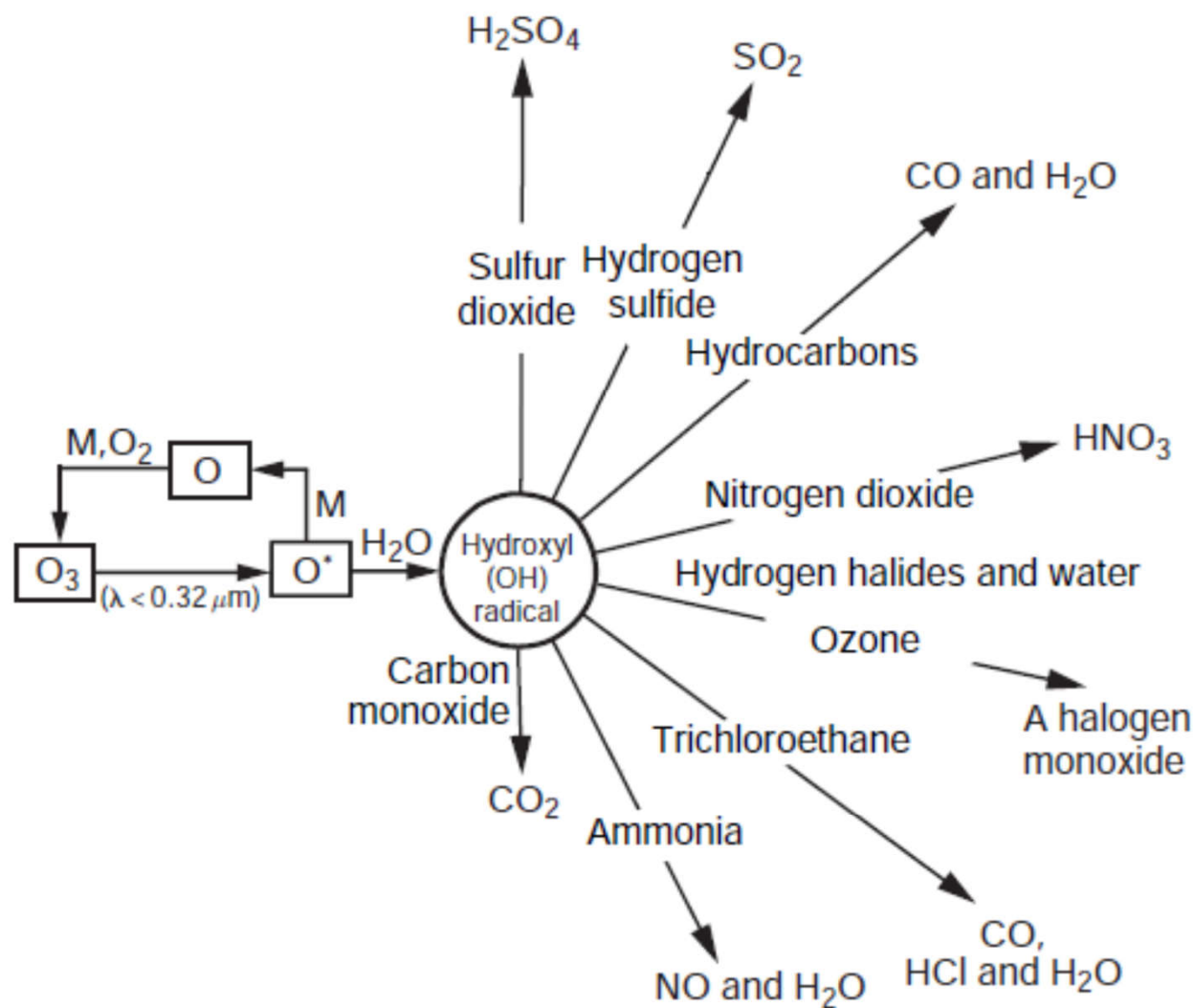


Fig. 5.4 Illustration of the central role of the OH radical in the oxidation of tropospheric trace gases. Little escapes oxidation by OH. [Adapted from *Global Tropospheric Chemistry*,

Bilans azotu

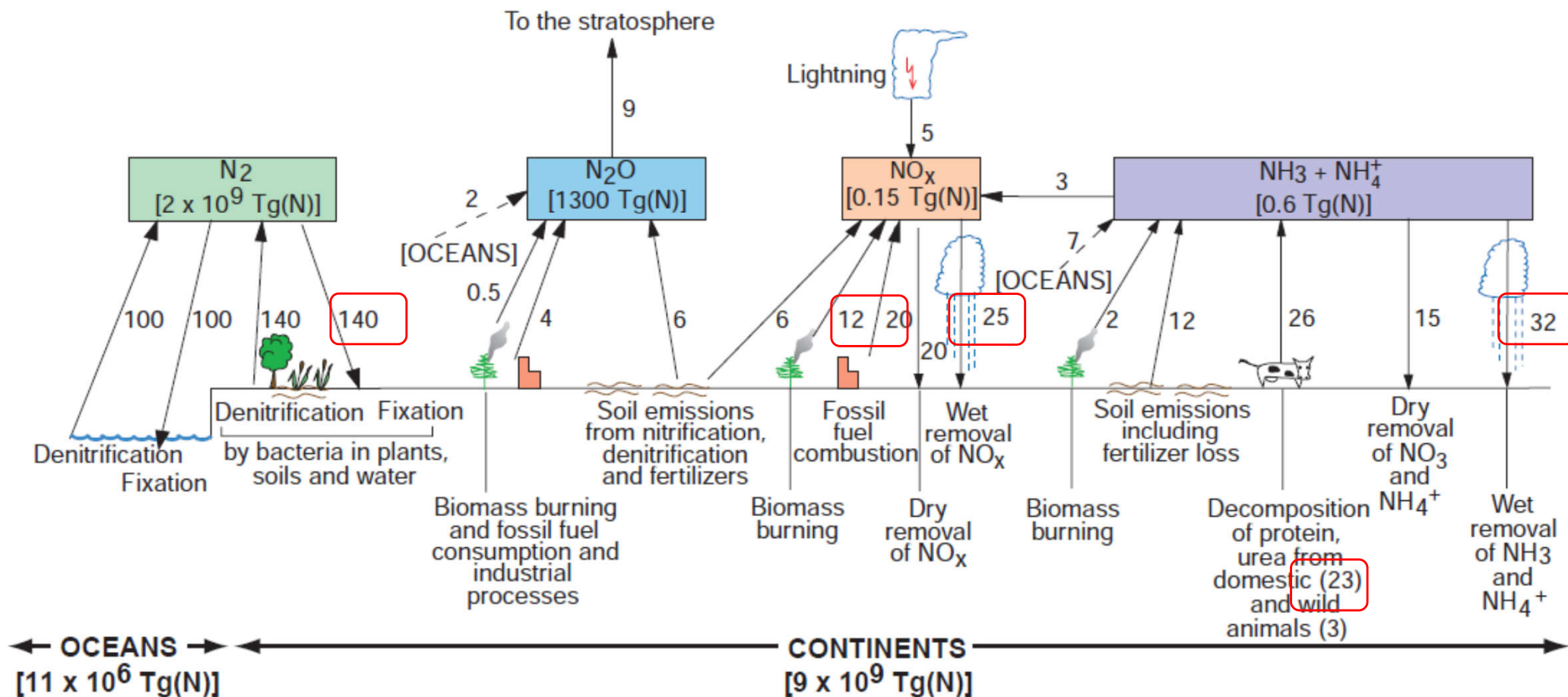


Fig. 5.14 Principal sources and sinks of nitrogen-containing gases in the atmosphere. Numbers alongside the arrows are estimates of average annual fluxes in Tg(N) per year; various degrees of uncertainty, some quite large, are associated with all of the fluxes. Numbers in square brackets are total amounts 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

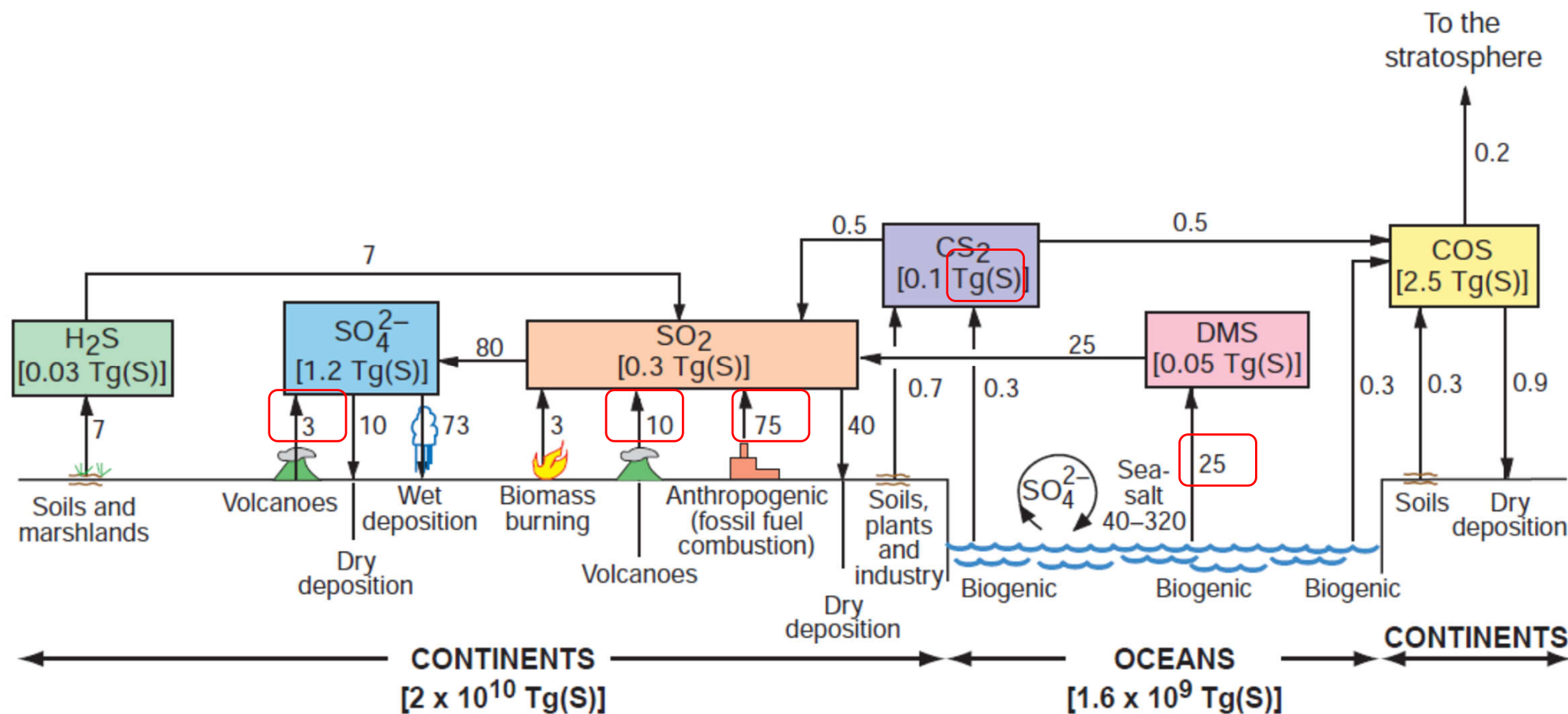


Fig. 5.15 As for Fig. 5.14 but for sulfur-containing species in the troposphere. Fluxes are in Tg(S) per year. For clarity, wet and dry removal are shown only over the continents, although they also occur over the oceans. [Adapted from P. V. Hobbs, *Introduction to Atmospheric Chemistry*, Camb. Univ.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

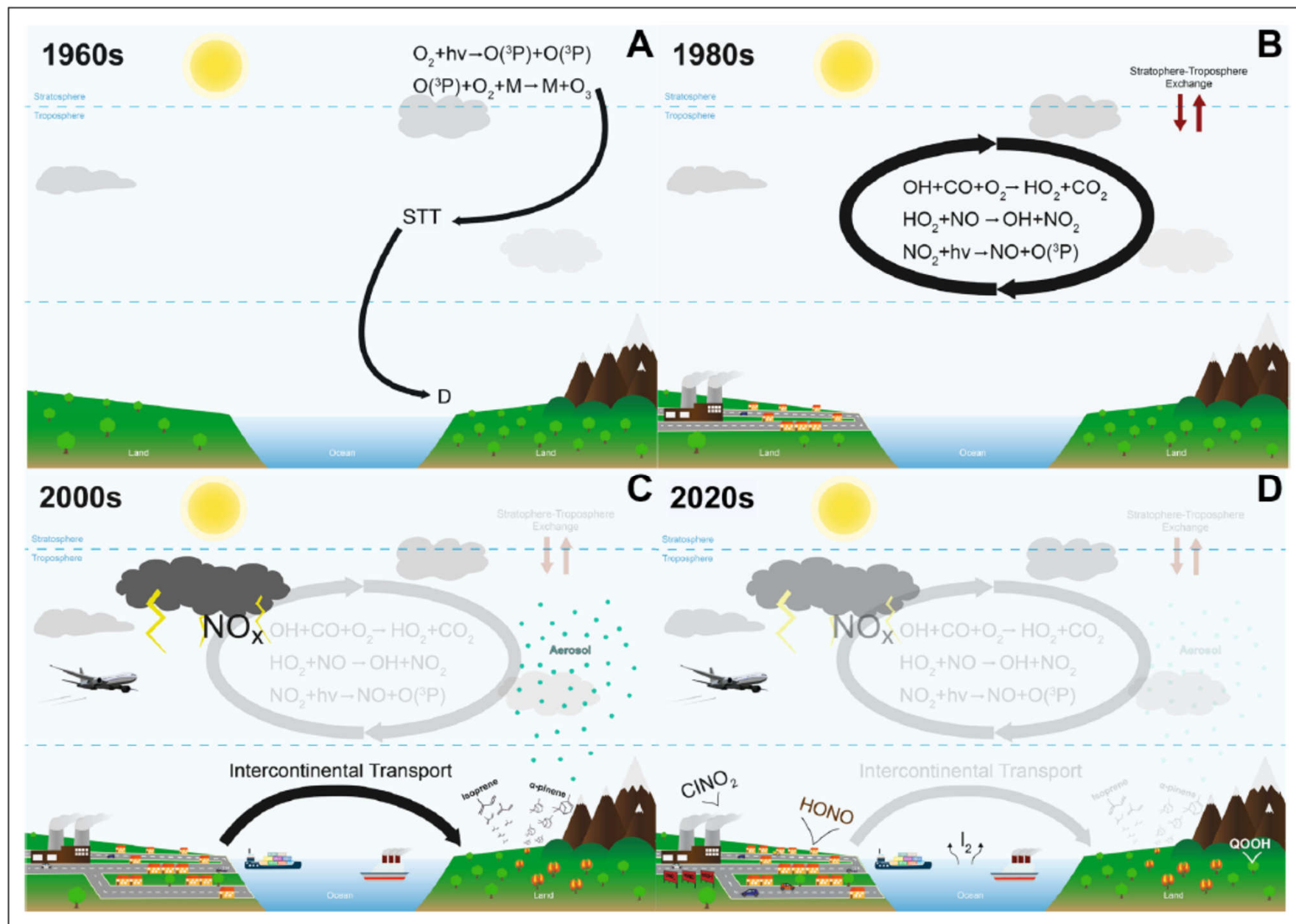


Figure 1. Schematic illustration of how our understanding of the chemical and physical processes controlling tropospheric ozone has evolved. The panels highlight the key processes identified in the different time periods. The labeling of dates in the subpanels (A–D) is indicative. DOI: <https://doi.org/10.1525/elementa.2020.034.f1>

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>

Art. 8(1), page 6 of 53

Archibald et al: TOAR-Ozone Budget

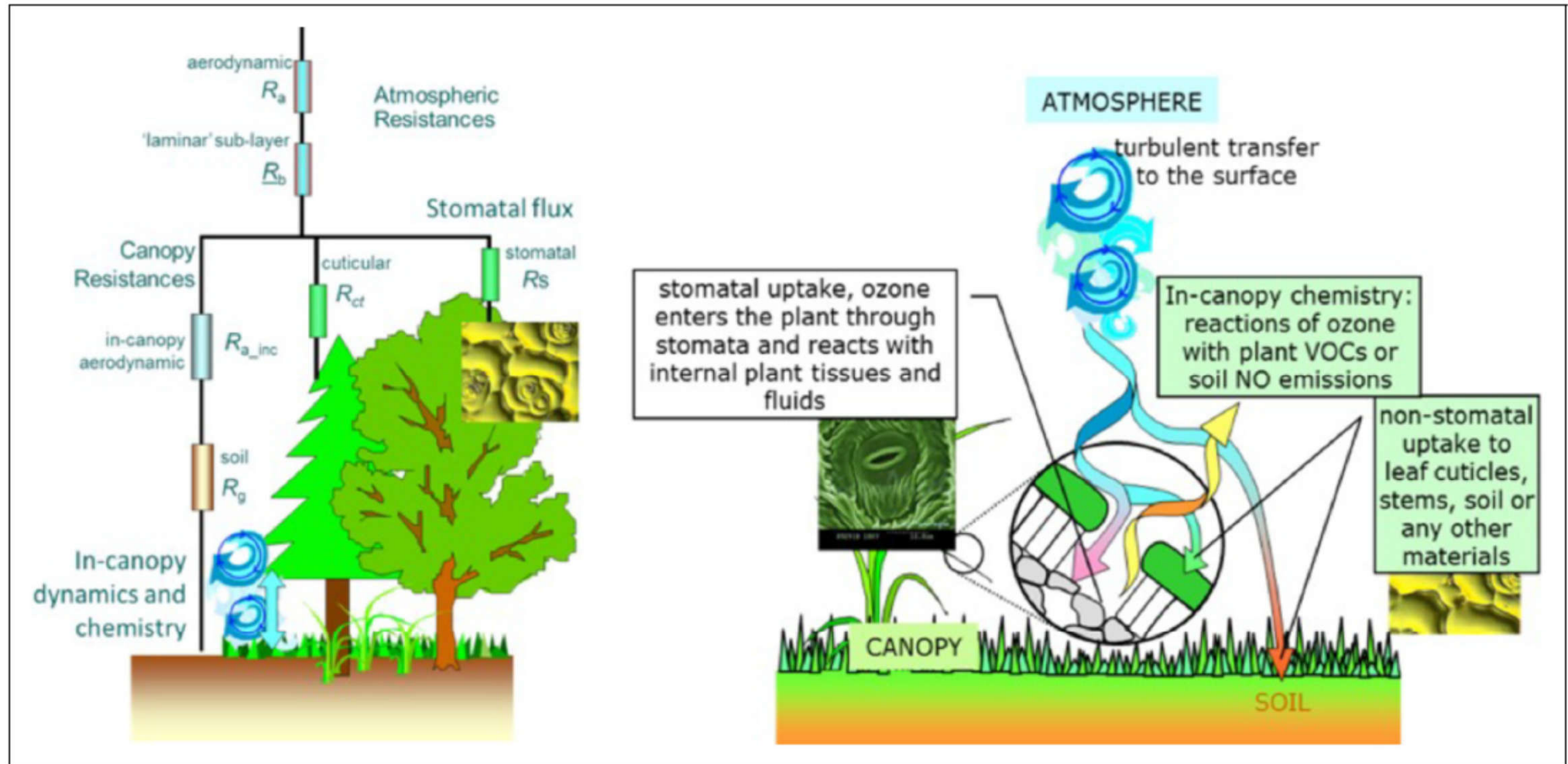


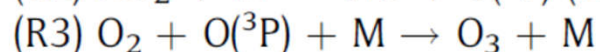
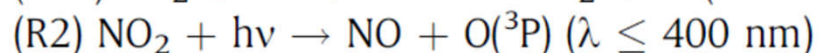
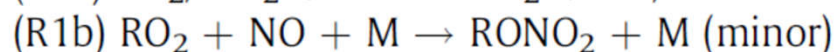
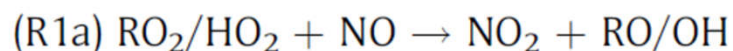
Figure 2. Pathways of ozone deposition on vegetated surfaces (with or without the resistance analogue used to quantify and model the processes). DOI: <https://doi.org/10.1525/elementa.2020.034.f2>

Bilans ozonu

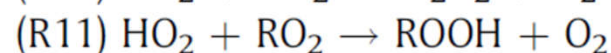
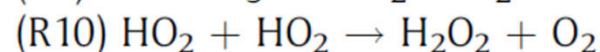
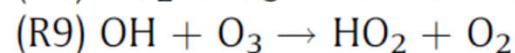
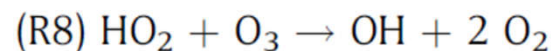
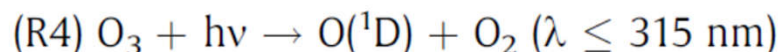
Archibald, A. T., et al. 2020. Tropospheric Ozone Assessment Report: A critical review of changes in the tropospheric ozone burden and budget from 1850 to 2100. *Elem Sci Anth*, 8: 1. DOI: <https://doi.org/10.1525/elementa.2020.034>

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 .

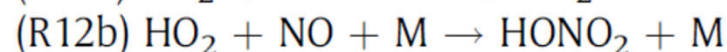
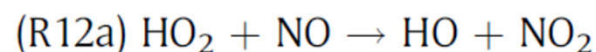


RO_2/HO_2 are organic peroxy radicals (R refers to an alkyl, aryl, or alkenyl group) and the hydroperoxy radical, respectively. These compounds are key intermediates in the production of ozone in the troposphere (see Section 5.5 for more details) as they convert NO into NO_2 without destroying ozone. 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.

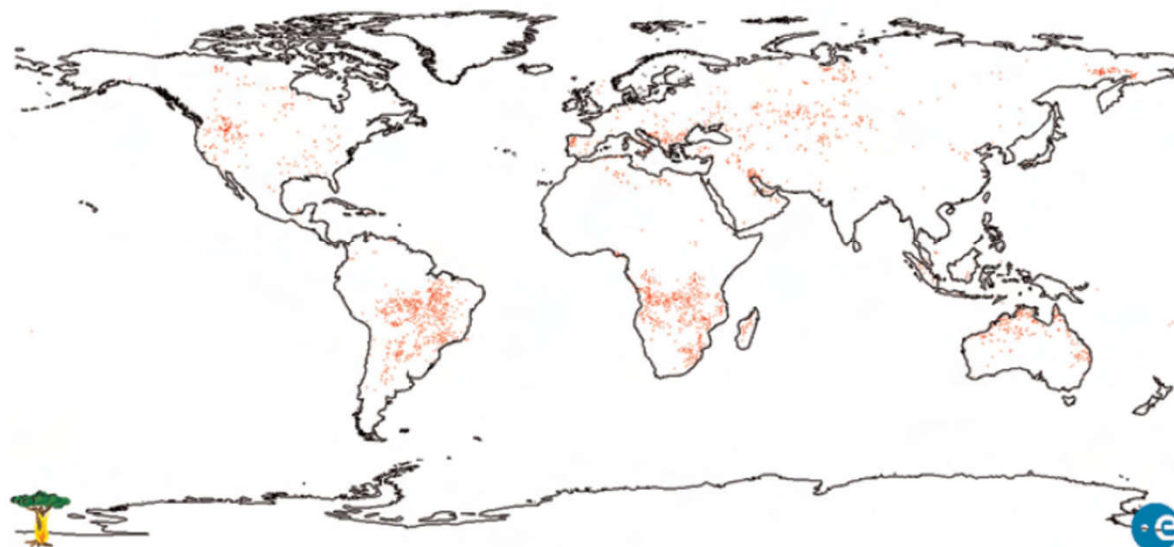


In addition to these chemical sinks of ozone, there are a number of physical sinks of ozone—deposition to surfaces (see Section 2.1) and uptake (including of oxidant reservoirs) onto particles (see Section 5.6)—that remove ozone from the troposphere.

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_x 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.



Ozon w troposferze



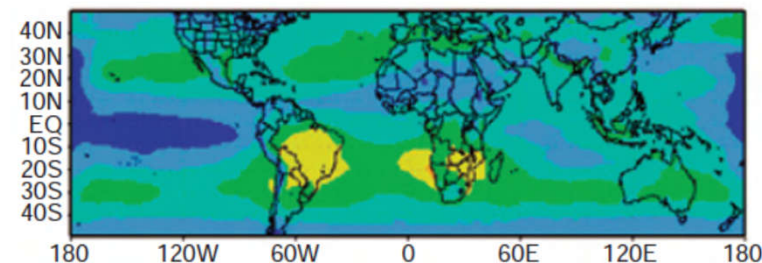
Global distribution of fires detected by satellite in September 2000. [Image courtesy of European Space

Smuga ozonu znad Afryki (wiosną) pochodzi ze spalania biomasy

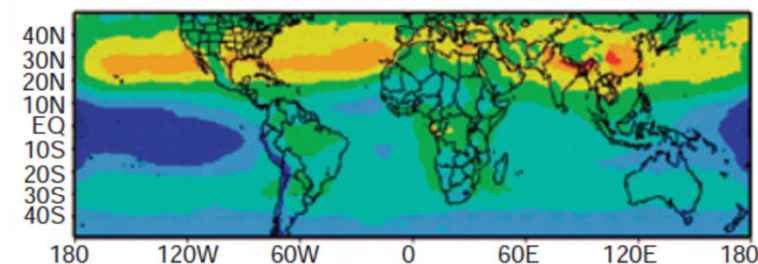
Podobna smuga nad Azją i Ameryką Płn., latem

Atmos. Chem. Phys. 3 895 (2005)

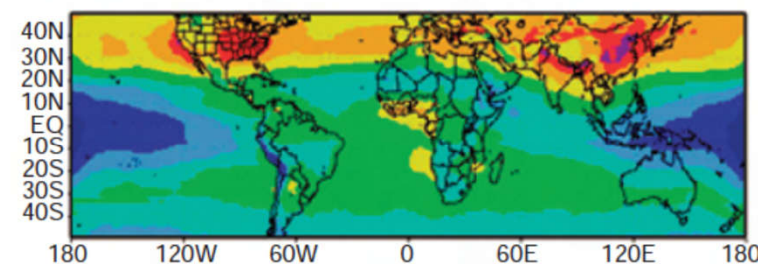
December–February



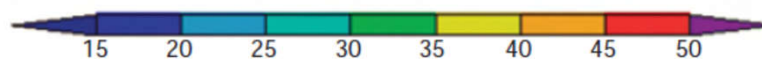
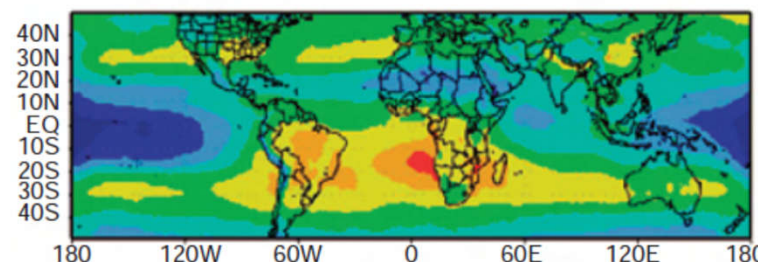
March–May



June–August

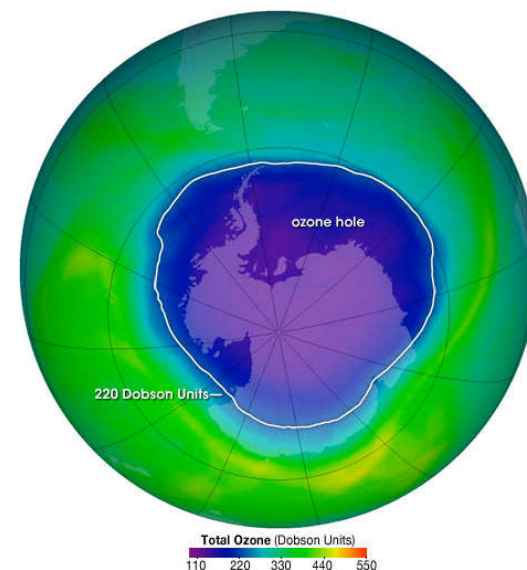
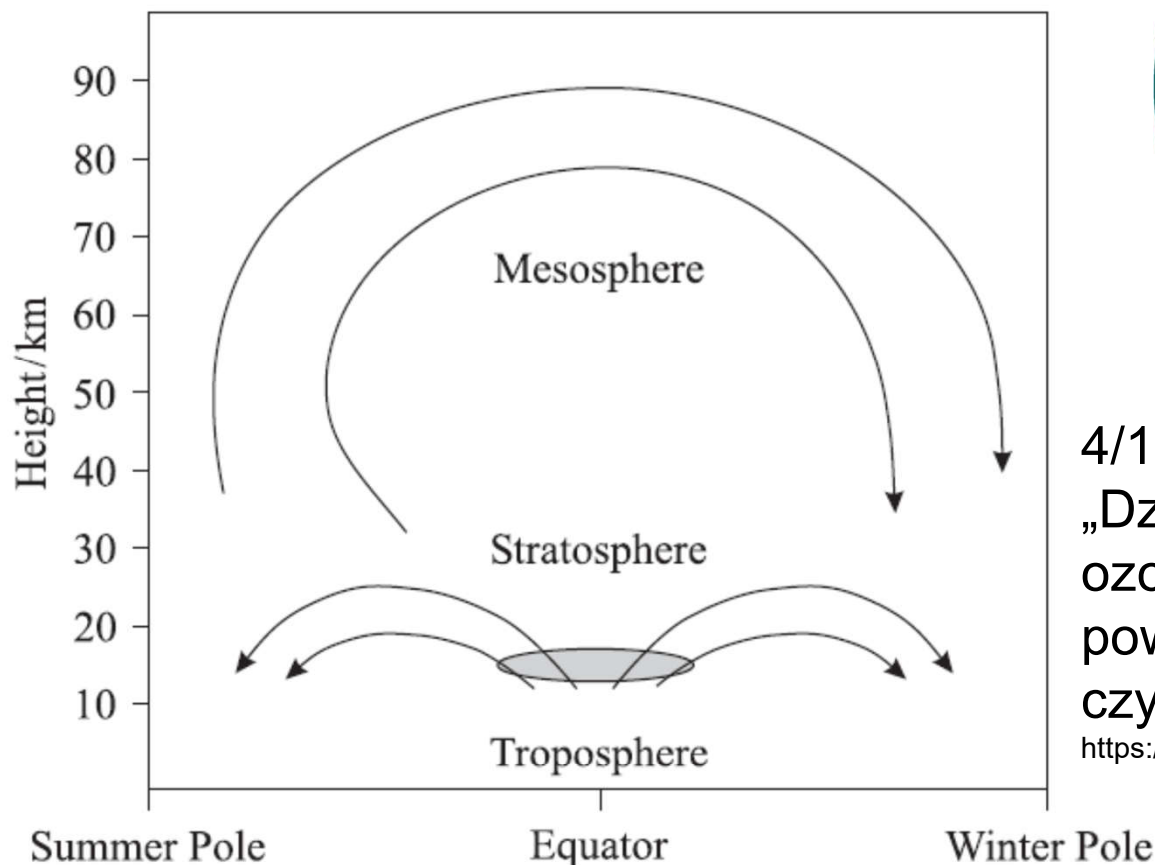
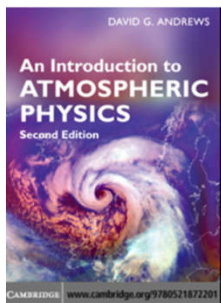


September–November



Dobson Units (DU)

Powstawanie i transport ozonu



4/10/2004

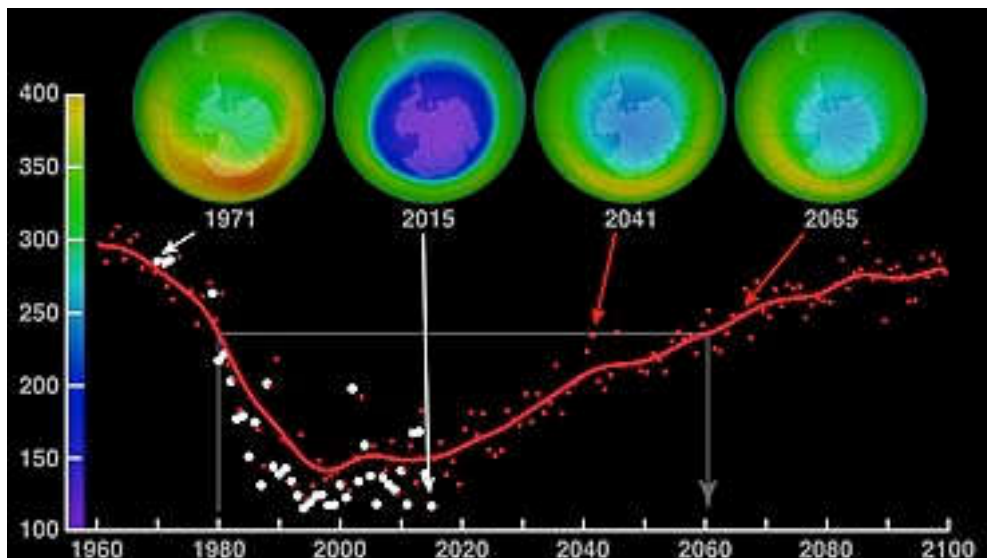
„Dziura” ozonowa oznacza, że ozonu jest mniej tam, gdzie powinien być jego rezerwuar, czyli nad Antarktydą

https://ozonewatch.gsfc.nasa.gov/facts/hole_SH.html

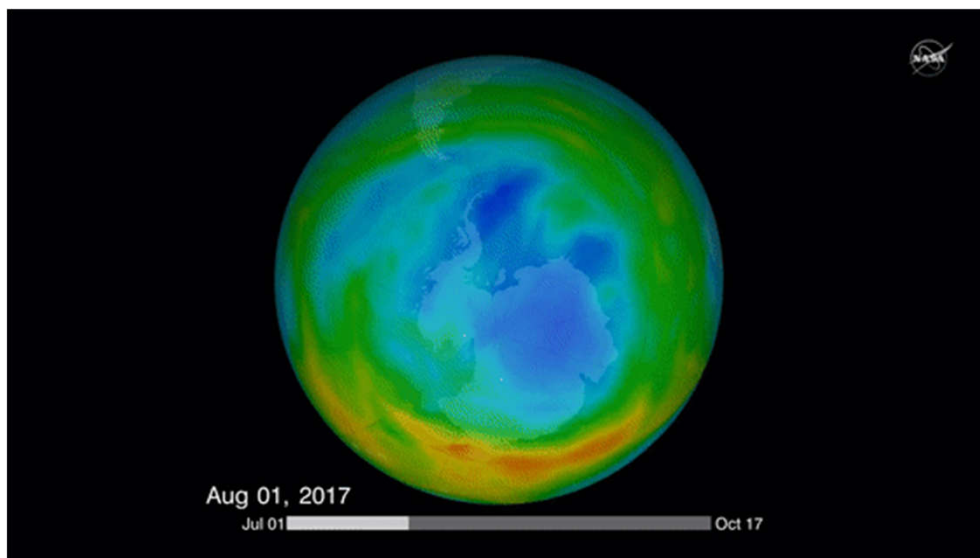
A schematic plot of the Brewer-Dobson circulation (lower four arrows, in the stratosphere) and the solstitial mesospheric circulation (upper two arrows). The shaded ellipse indicates the approximate position of the 200 K isotherm near the equatorial tropopause, i.e. the 'cold trap' identified by Brewer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

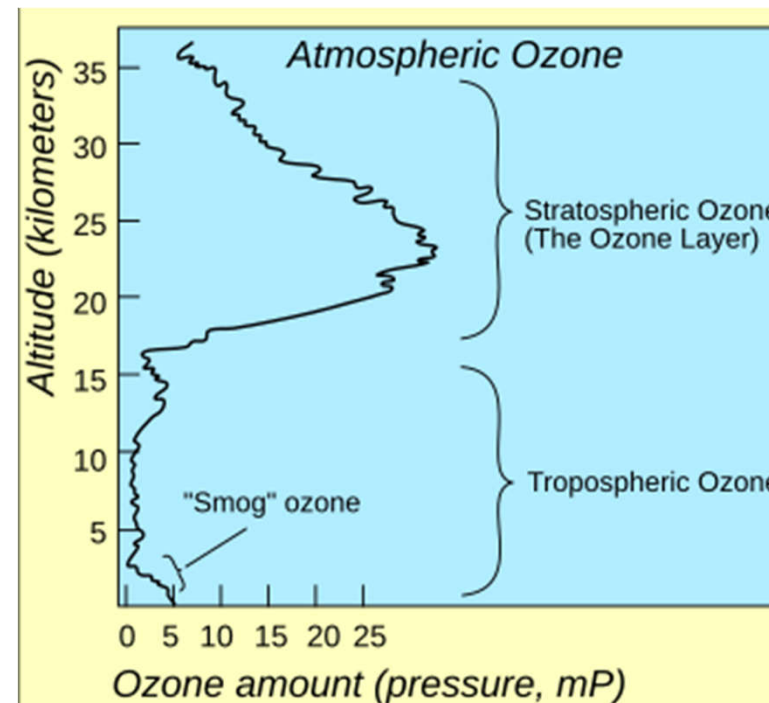
„Dziura” ozonowa nadal istnieje, ale powoli się zablężnia



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

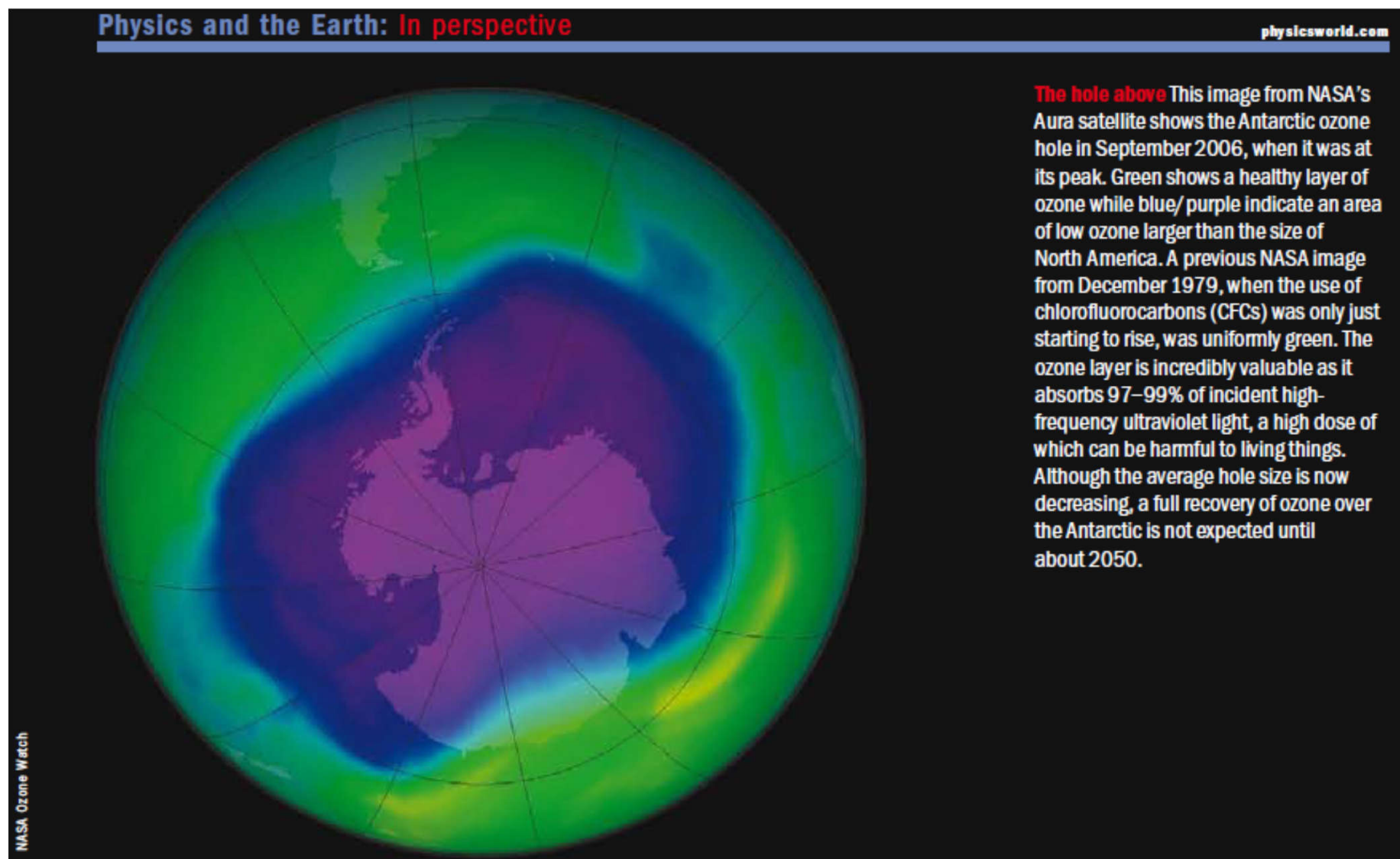


<https://www.nbcnews.com/mach/science/good-news-about-ozon-hole-even-better-you-think-ncna835971>



„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 zablężnia się, ale potrwa to jeszcze dziesiątki lat.

Antroposfera



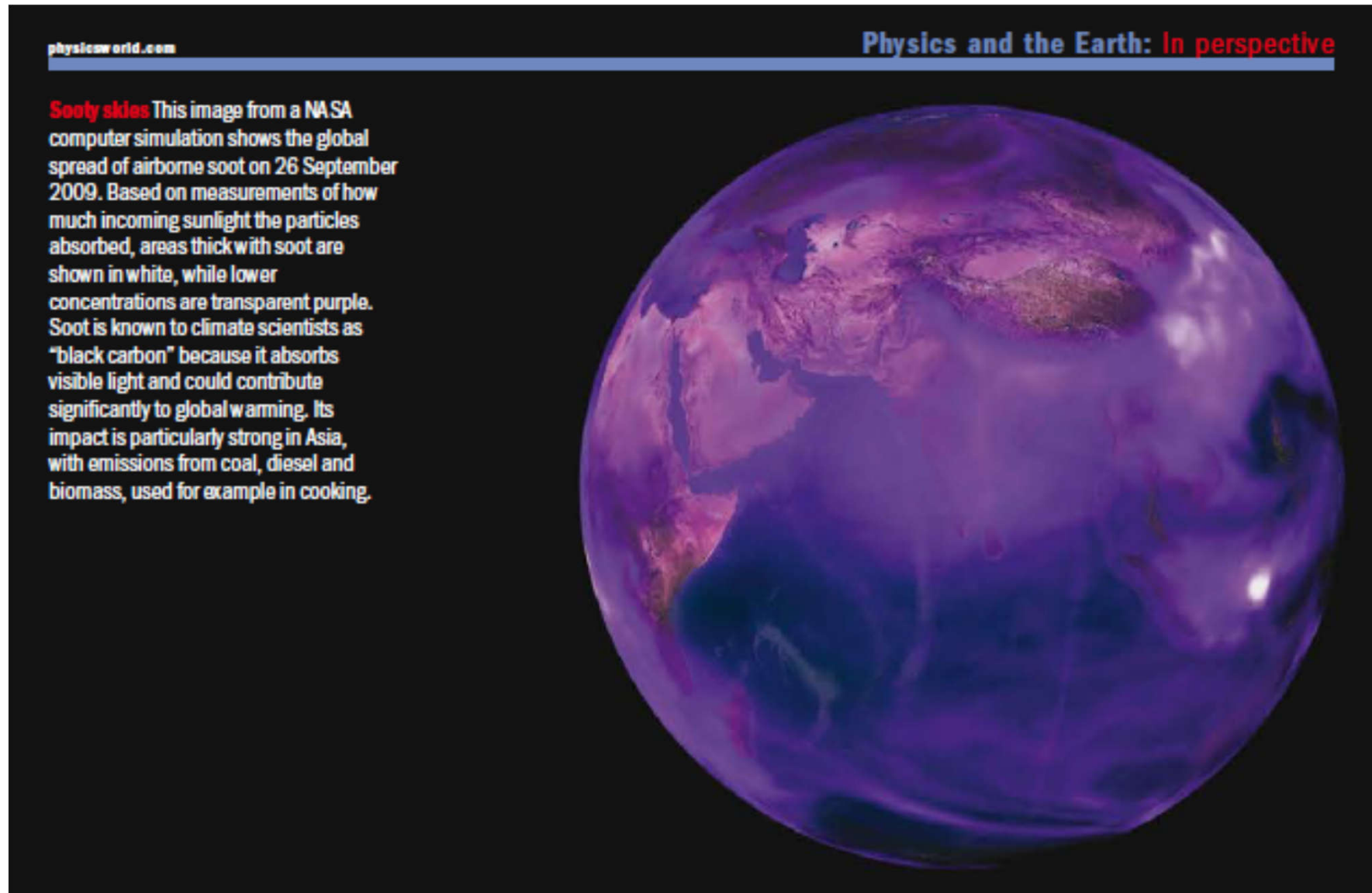
Półwysep Iberyjski (i stratosfera) nocą 4.12.2011 roku

Antroposfera



Delta Nilu nocą: „hałas” światel 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

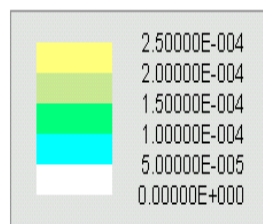
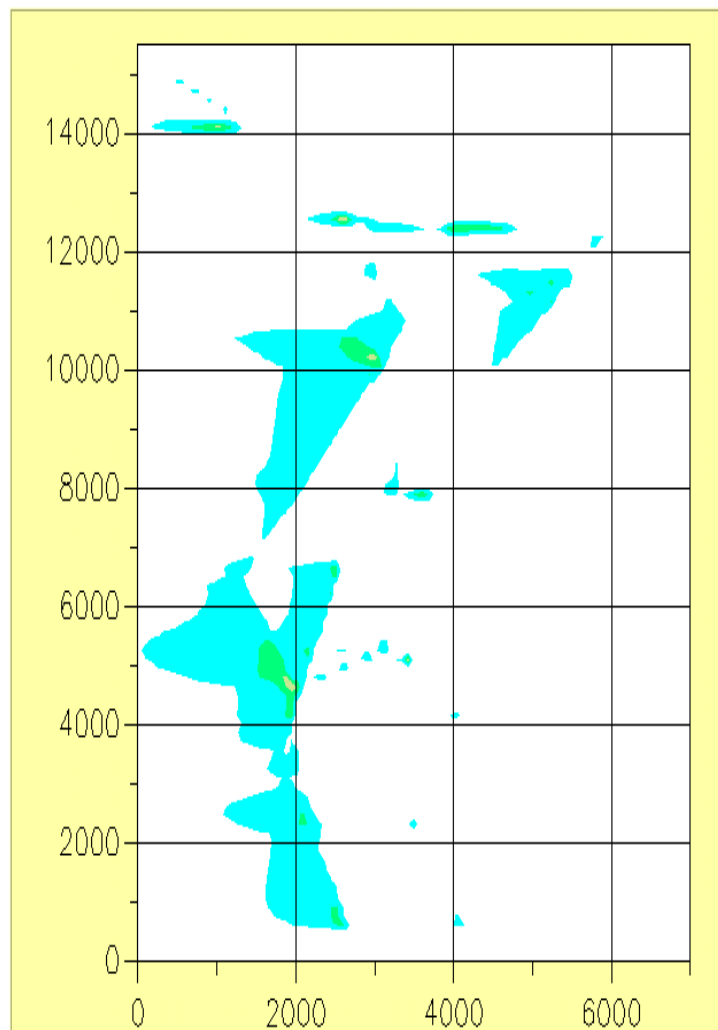


Zanieczyszczenie atmosferyczne (lokalne):

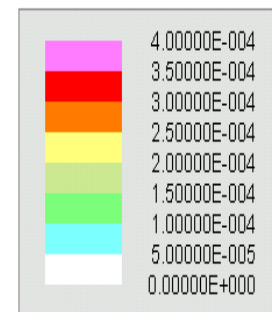
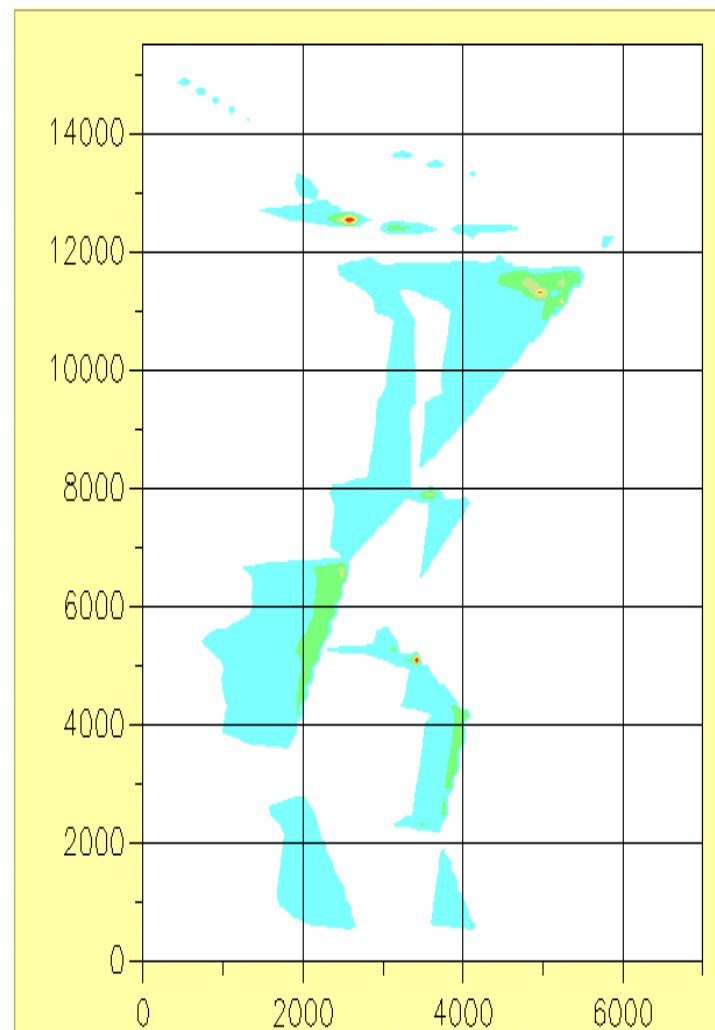
- Tlenek węgla CO 30 mg/m³
- Mikropyły (PM10) 150 µg/m³
- Tlenki azotu (NO, NO₂) 200 µg/m³
- Dwutlenek siarki (SO₂) 15 mg/m³
- ozon O₃ 180 µg/m³ (dla roślin 150 µg/m³)
- Węglowodory (benzen) 15 µg/m³

Modelowanie zanieczyszczeń = prevencja

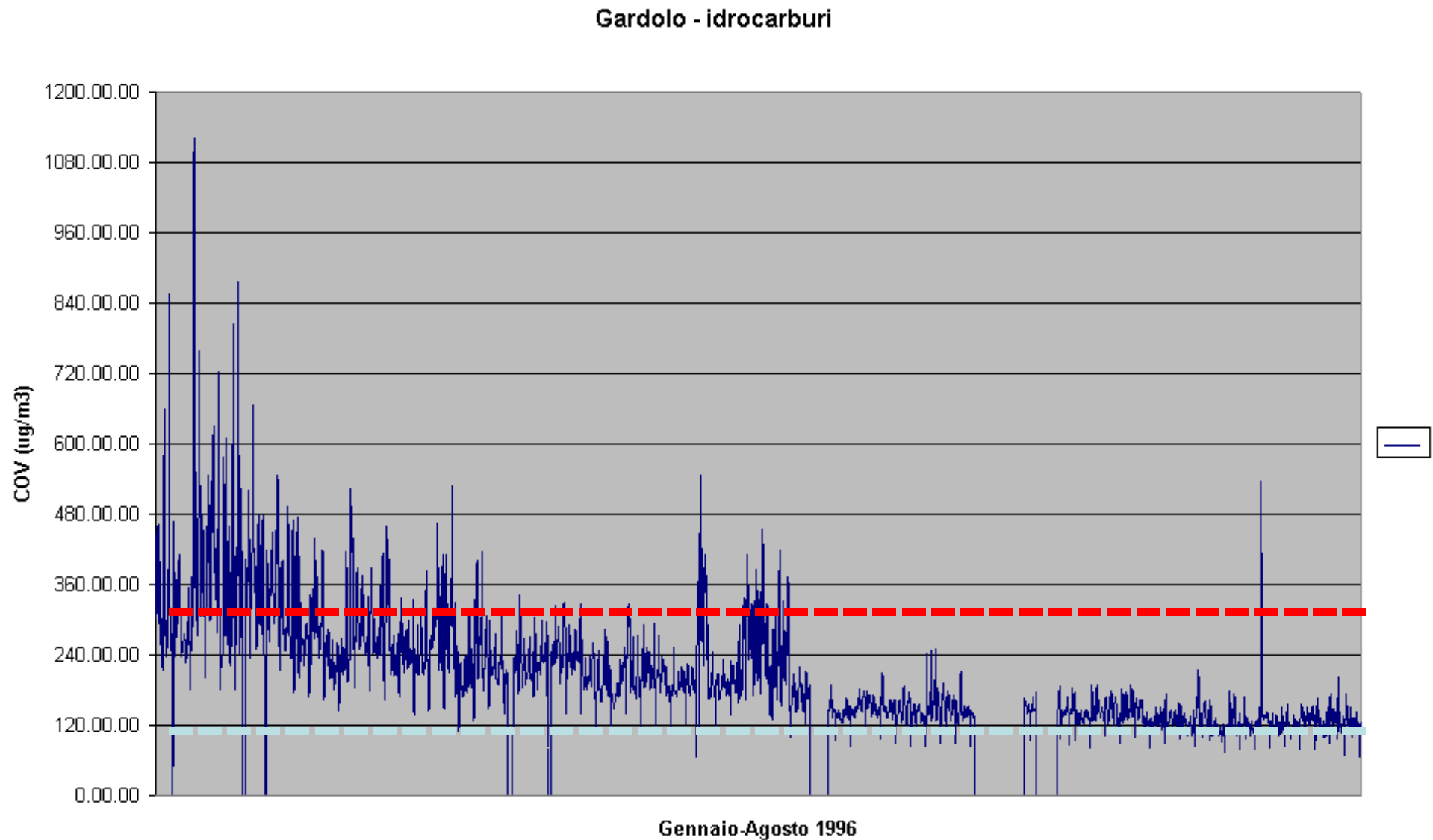
Viabilità attuale



Traforo Mezzolombardo



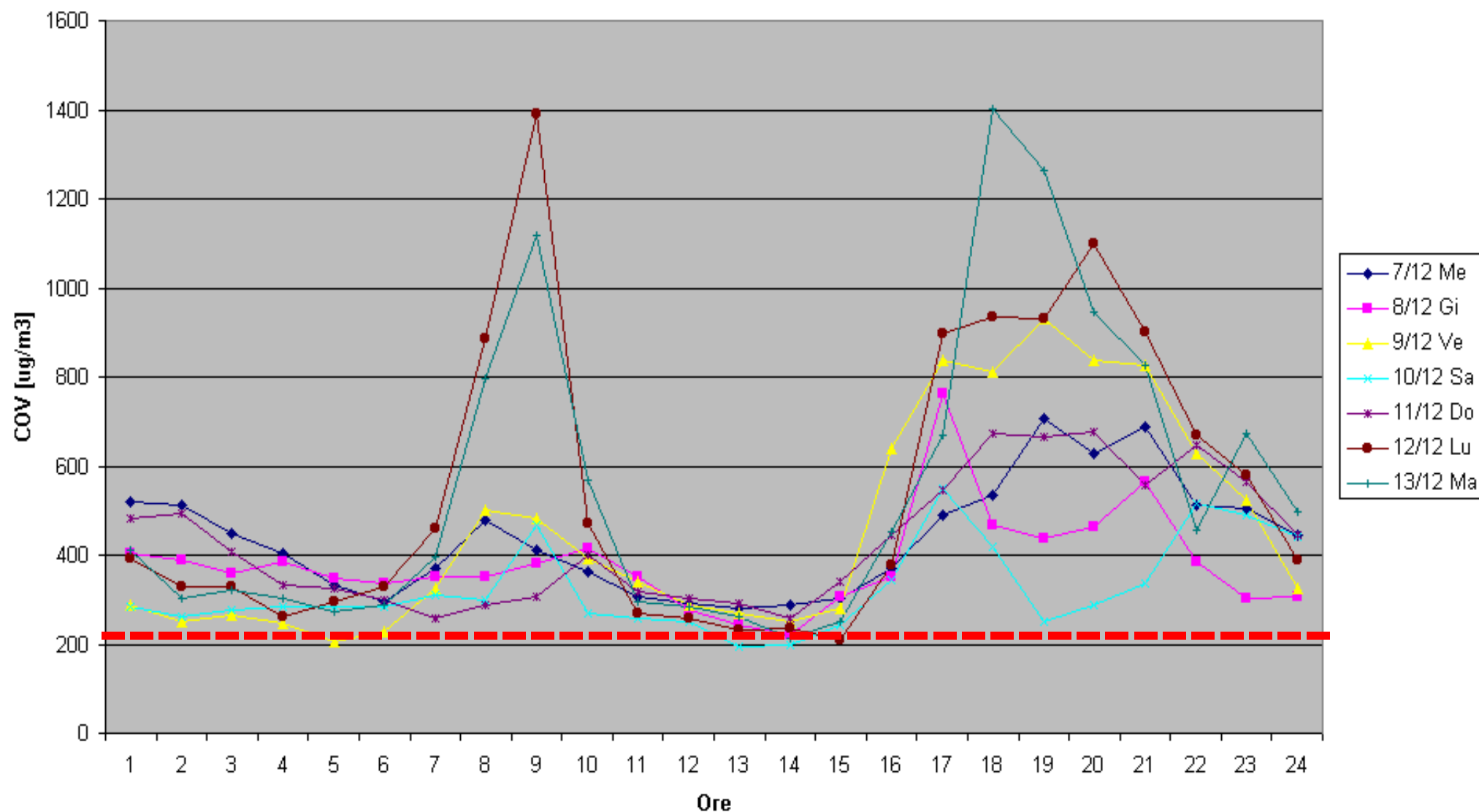
Zanieczyszczenie lokalne (węglowodory)



Analiza: GK

Zanieczyszczenie lokalne (węglowodory – ruch drogowy)

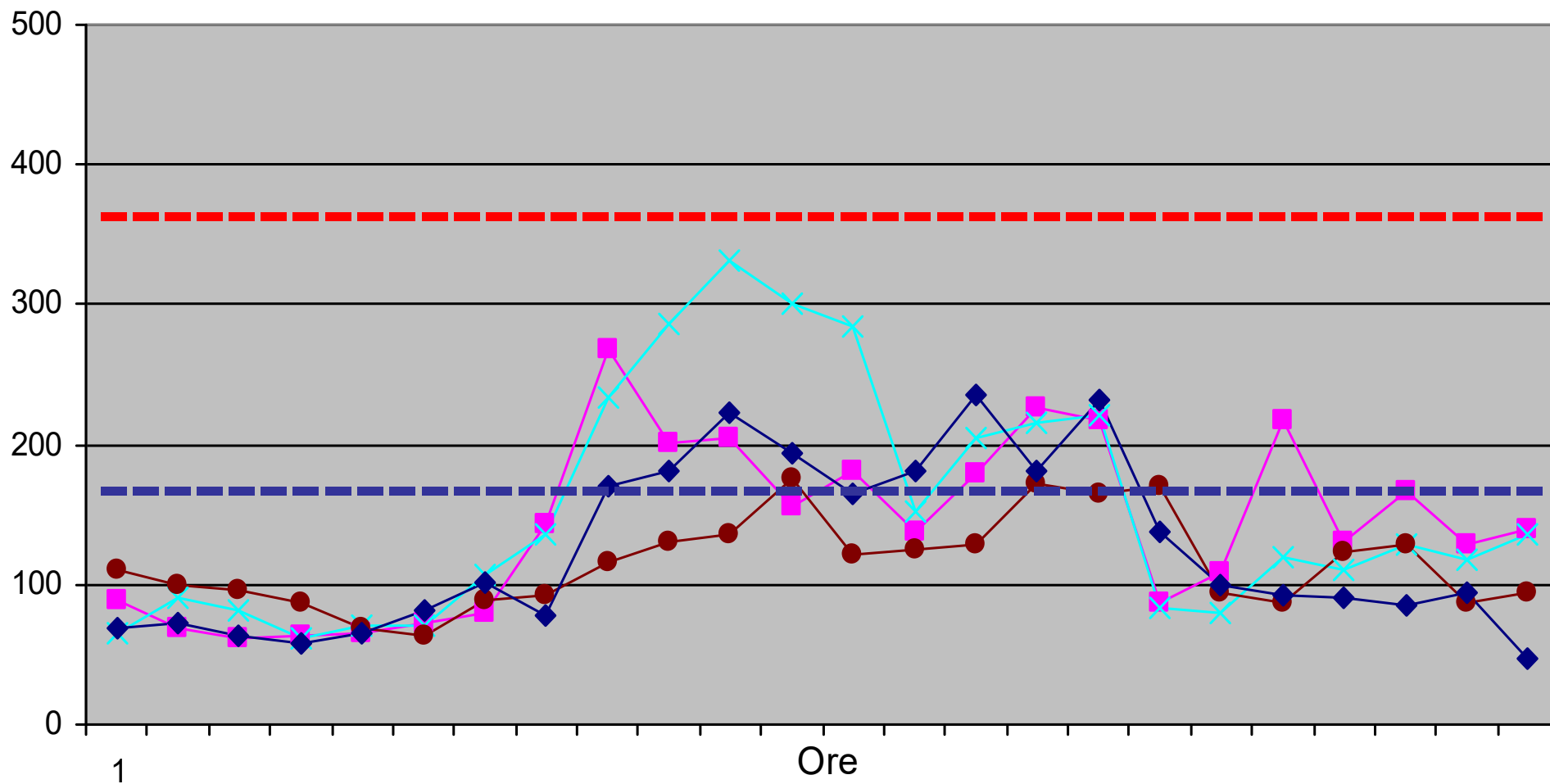
Lavis 1994 - Idrocarburi



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

Zanieczyszczenie localne – dwutlenek azotu

Lavis - Biossido di azoto





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



„Polska w czołówce krajów

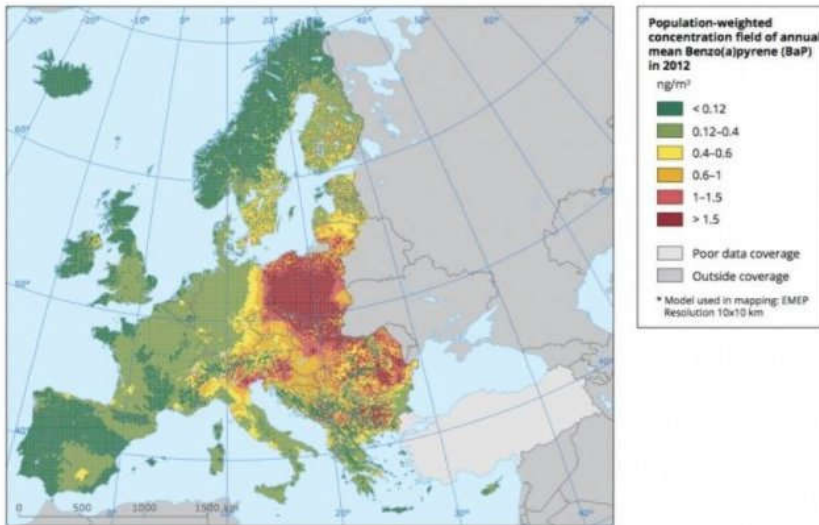
zanieczyszczających powietrze w Europie”

Polska na czele krajów
zatrzuwających powietrze
w Unii Europejskiej

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

Stężenie benzopirenów w powietrzu

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



Źródło: Komisja Europejska. Dane z 2012 roku



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.

REKLAMA
REKLAMA

3. Kraków

...

10. Katowice

Izba powołała się na dane OECD, które wskazują, że 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)

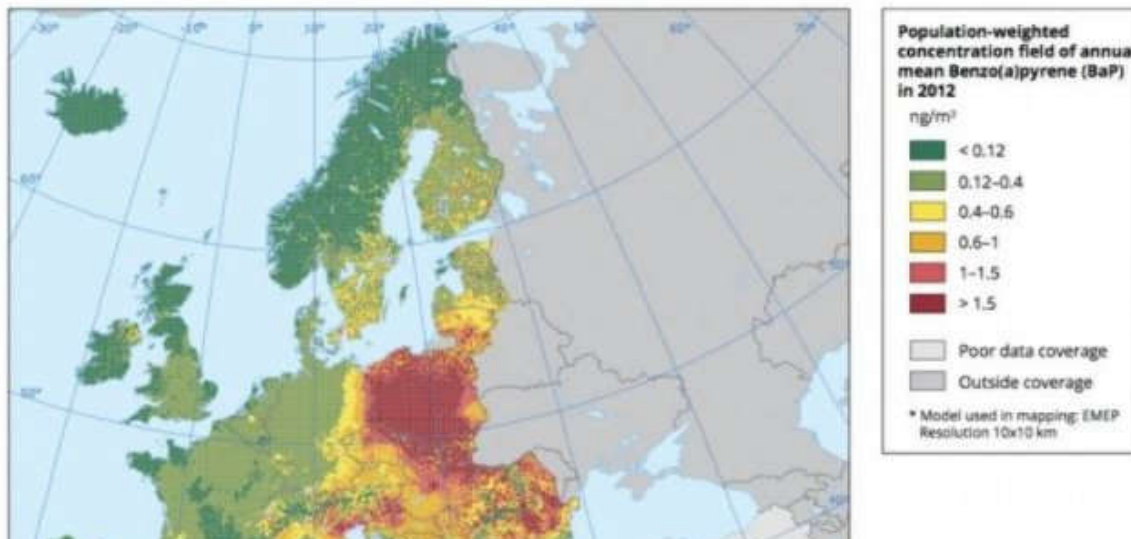
FOCUS.pl



1/2



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



Polska na czele krajów
zatrzuwających powietrze
w Unii Europejskiej

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

Stężenie benzo(a)pirenu 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 przekroczone 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

← → ↺ ⓘ www.sciencedirect.com/science/article/pii/S0160412010002278?via%3Dihub

☰ Outline



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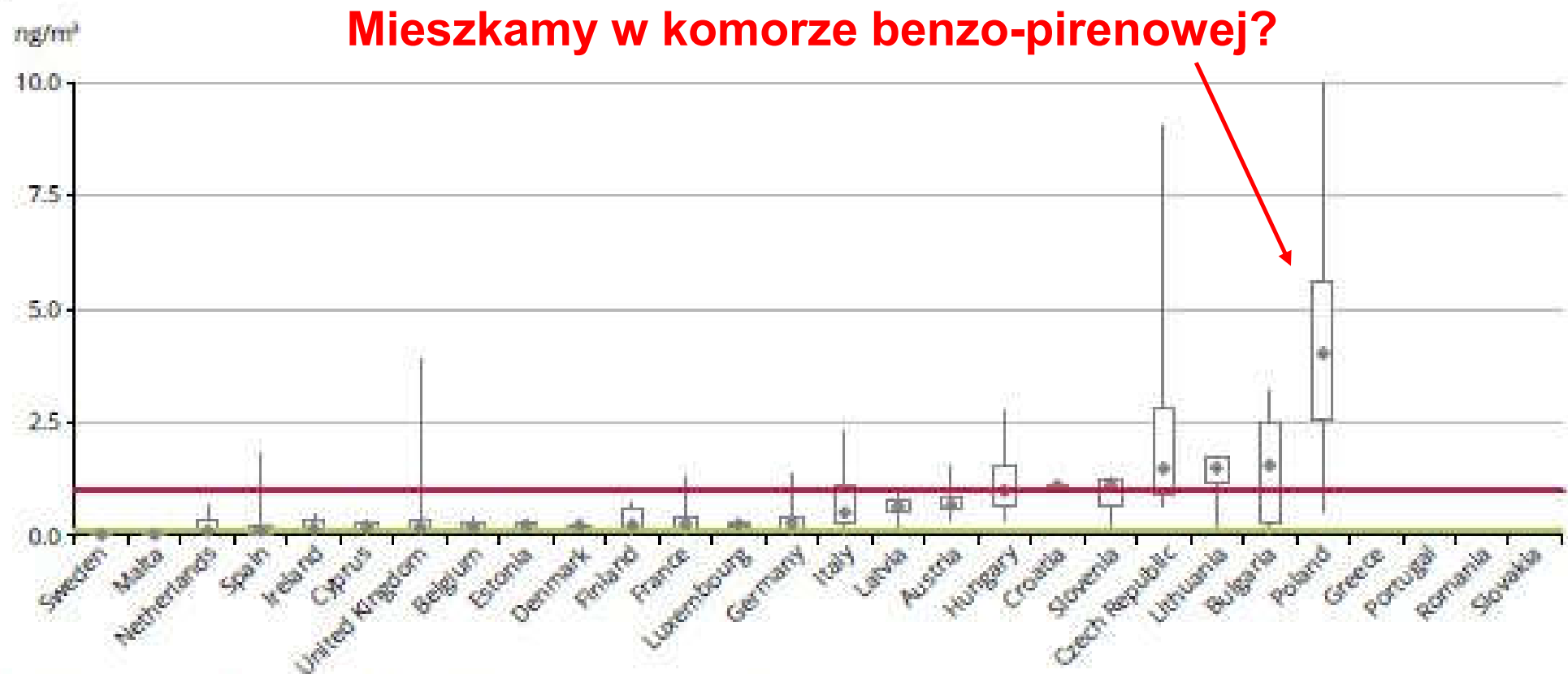
exposure (Maynard et al., 1997). PAH=poli-aromatic-hydrocarbons

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 $\mu\text{g}/\text{m}^3$ 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 $\mu\text{g}/\text{m}^3$ 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/m³

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).

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Thanks to dr Daniela Ascenzi