- **Problem of man-made Sulphur is**
- **very actual for air quality in Russia**
- **NEW environmental law** of Russian Government is:
- **since 1 July 2006 :**
- **Suphur wastes by diesels must be**
- **lower on 38%**
- Benzene oil must be **without Pb** addition

# Sunlight action on the oxidation SO2 into sulphate aerosol affecting the climate and ecology of the Earth

Galina Skubnevskaya,
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Alex Ankilov
Alex Kozlov
Galina Dultseva

RFBR Grant 02-05-64783

- Global Sulphur cycle
- Man-made stress for Earth
- Ways of SO2 transformation to H2SO4
- About role of exited SO2 in the atmosphere
- Some results of study of exited SO2 (1980-2005)

  (Photolysis and Photonucleation )
- Some conclusions and plans for future

# Global sulphur cycle



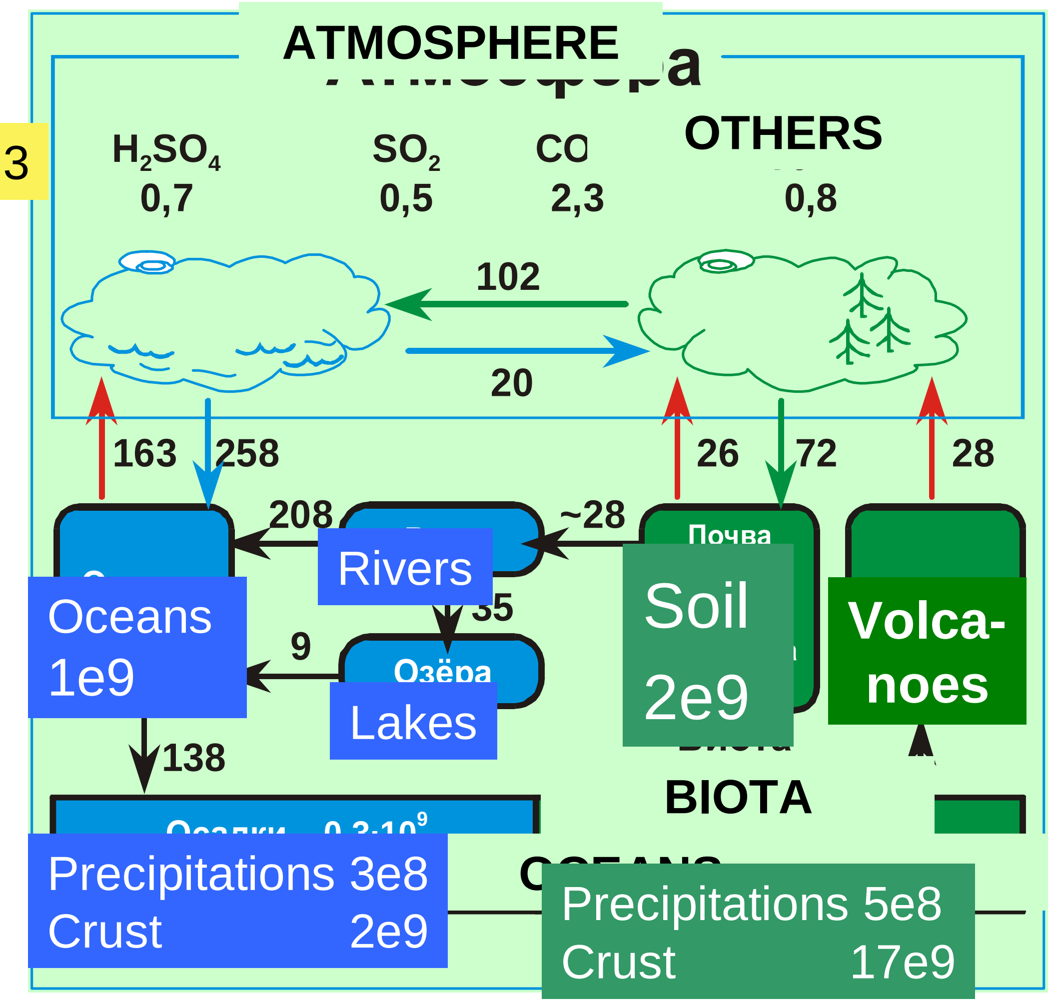
In the air over Baikal lake

**Sulphur flow is ~ 3-5 tonn/km$^2$year**

**Acidity of rains and snow << 5,6 pH**

**East Siberian forests are in danger**

g/m3

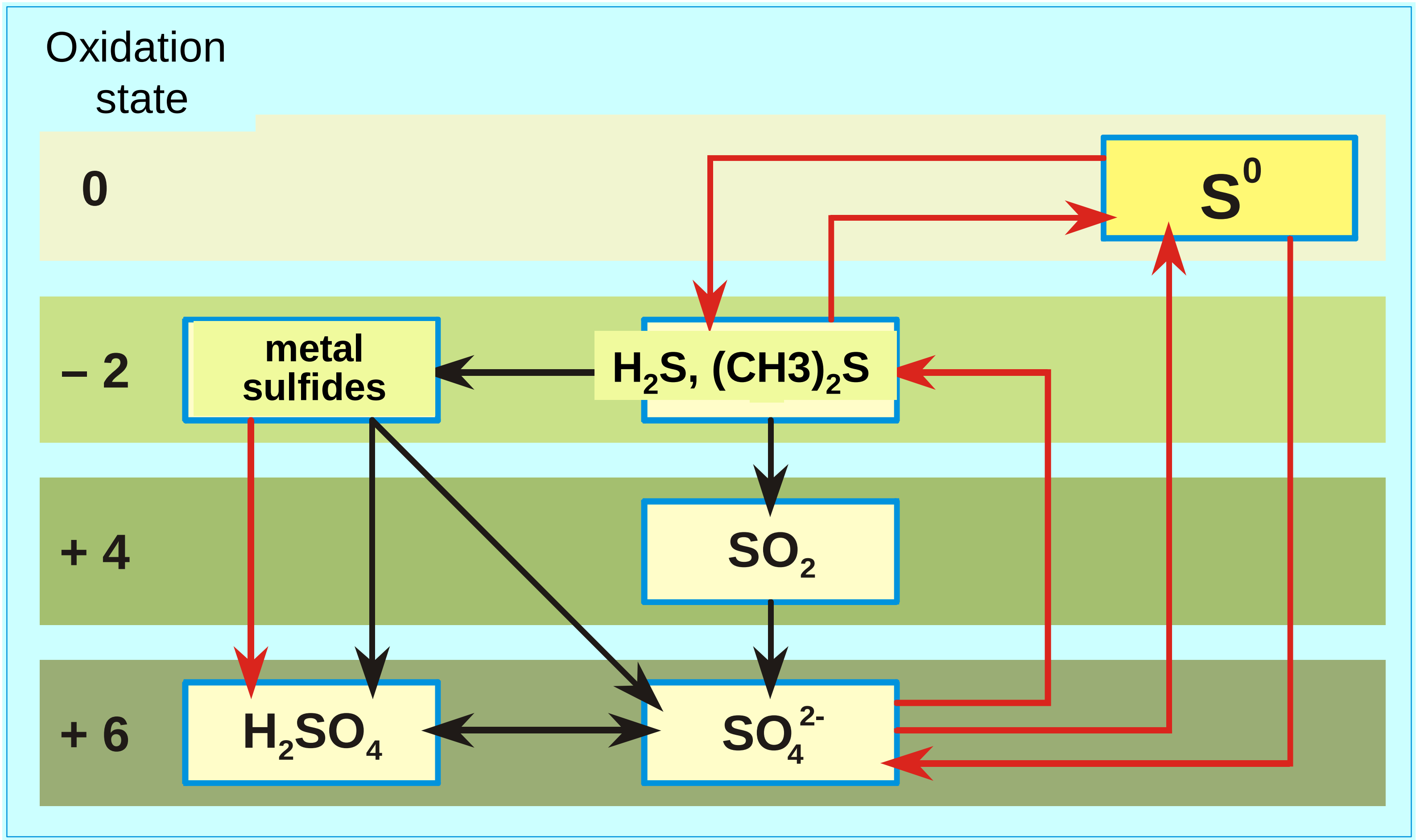



**<u>Reservoirs (Gt):</u>**

| | |
|---|---|
| **Crust** | **19000000** |
| **Sedimentary rock** | **5000000** |
| **Oceans** | **13000000** |
| **Soil** | **260** |
| **Living organisms** | **0.76** |
| **Atmosphere** | **0,004** |

**Sulfur distribution (Mt) on the Earth surface and Sulfur flows (Mt/year)**

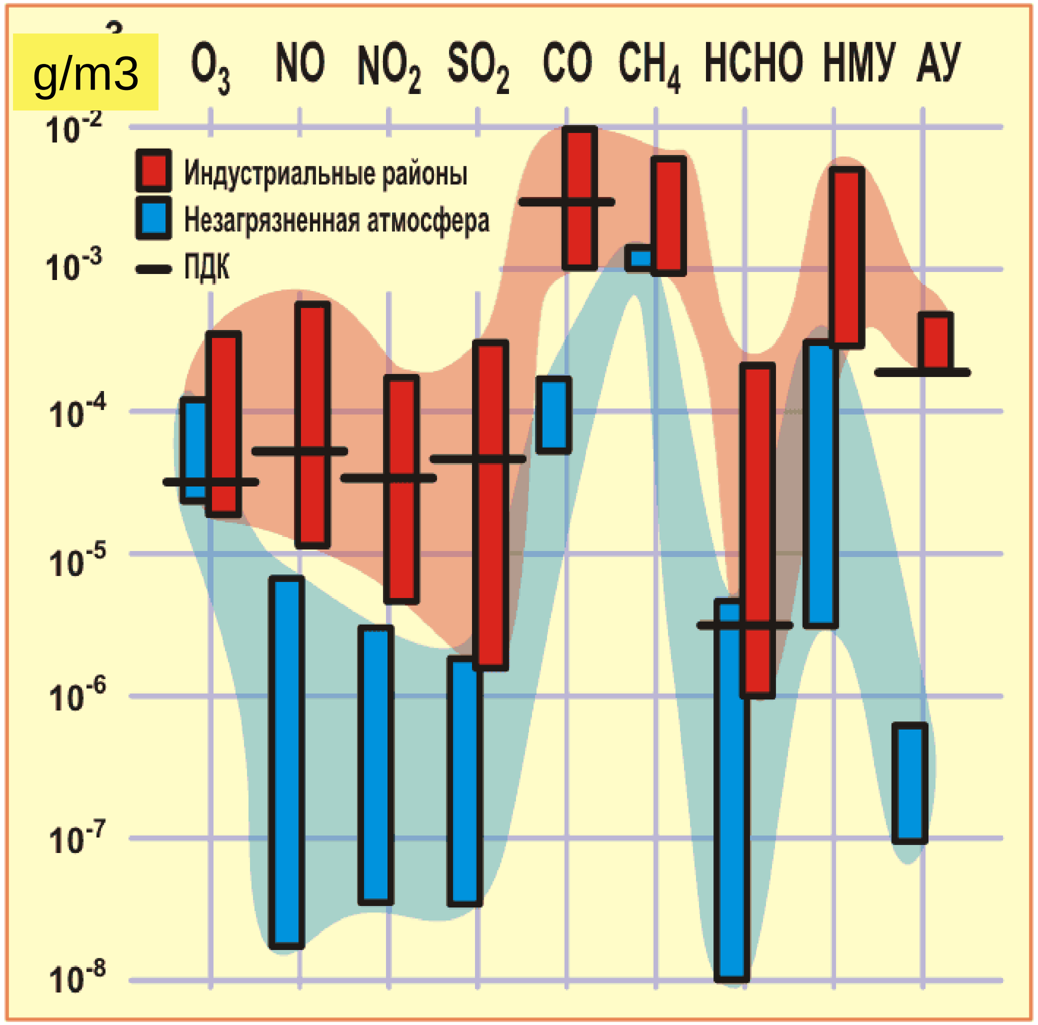
# Oxidation state of S changes in Global cycle




Red arrows – microbiological processes

# In XXI century Emission of S from Man-made sources became comparable with Natural ones

| | Content, $ppb^{-1}$ | |
|---|---|---|
| | Remote regions | polluted air |
| $O_3$ | 20-80 | 100-500 |
| NO+NO2 | 0,1-0,5 | 50-750 |
| SO2 | 0,1-1 | 2-300 |
| Man-made hydrocar-bons | 1-5 | 500-1200 |
| aerosols | 3-10 $mkg/m^3$ | 50-70 $mkg/m^3$ |



# Acidity of rains ,snow and fogs < 5,6 pH is dangerous



## $SO_2$ influence on the acidity of atmospheric precipitations:

**Flow to the Earth surface**

| | Residence time, hour | | |
|---|---|---|---|
| | **$SO_2$** | **$H_2SO_4$** | **$SO_4^{2-}$** |
| **Oxidation** | **37** | – | – |
| **Neutralization** | – | **50** | – |
| **Washing out** | **100** | **83** | **70** |
| **Dry deposition** | **70** | **200** | – |

# Sunlight action on $SO_2$ generates ecological problems in Earth atmosphere

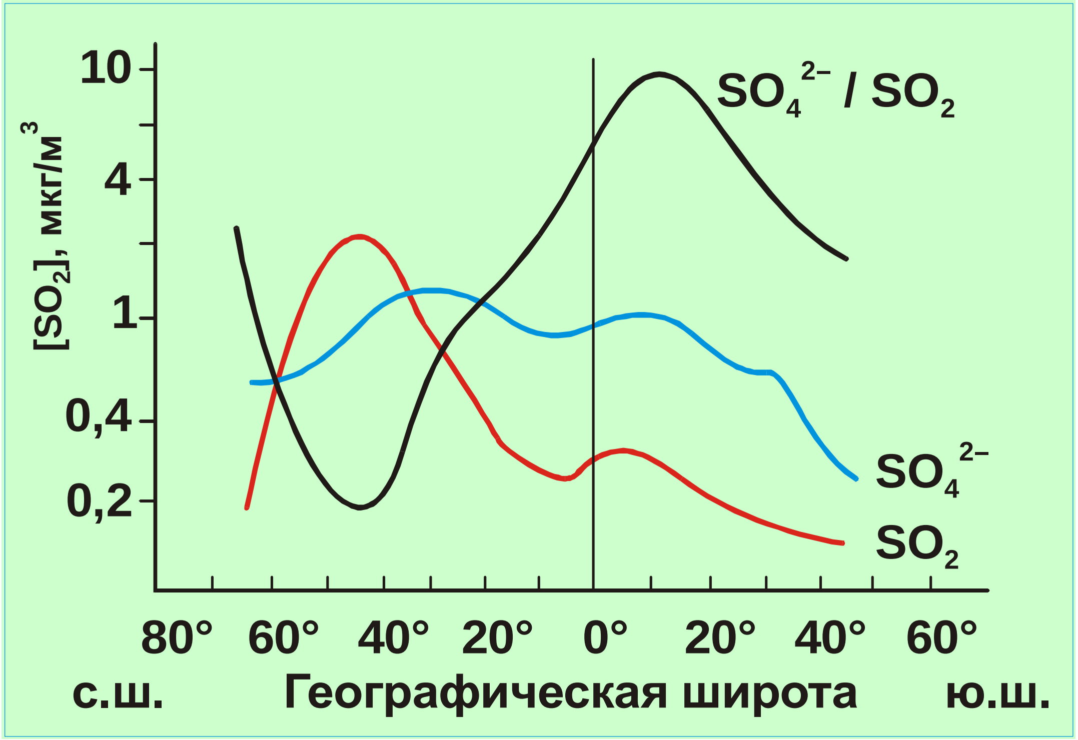
- **Sunlight action stimulates** transformations of primary S wastes into **ecotoxicants** in the air and in photosmog
- **Photosmog** includes toxicants and aerosols with S that **affect on lungs and health of citizens**.( $H_2S$, $(CH_3)_2S$, $SO_2$, $H_2SO_4$, organic sulphoacids in air and in aerosols)
- **Sulphate nanoparticles** in lower stratosphere (Junge layer on h~16 km) **affect climate** and fall of **acid rains**
- Photochemistry and **photonucleation of $SO_2$** is **unsolved global problem** in the Earth atmosphere.

# Typical Relation of SO4(2-)/ SO2 in the air



**At the surface of Earth**

| Substance | Remote regions | Urban areas | Cities |
|---|---|---|---|
| $SO_2$ (mcg/m$^3$) | ~0,2 | 0,1- 0,6 | 0,3-1 |
| $SO_4^{2-}$ (aerosol) (mcg/m$^3$) | ~0,8 | 0,2-0,5 | 1-5 |



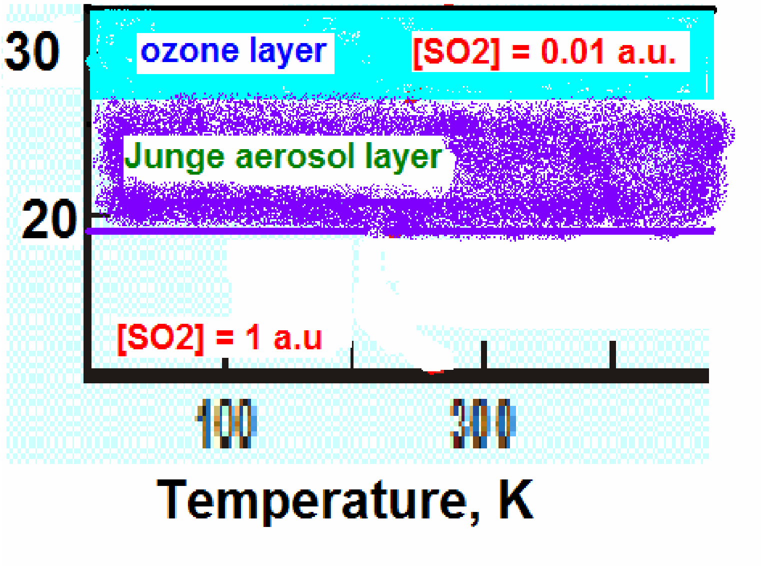

| | | | |
|---|---|---|---|
| $SO_4^{2-}$ (aerosol) /SO2>1 | is due to | SUNLIGHT | ACTION? |

# Chemical Ways of SO2 oxidation

- Reactions on soot and atmospheric particles ( **heterogenic oxidation**)
- Reactions in rains (**in liquid phase)**
- Reactions of photocatalysis by particles (ZnO )

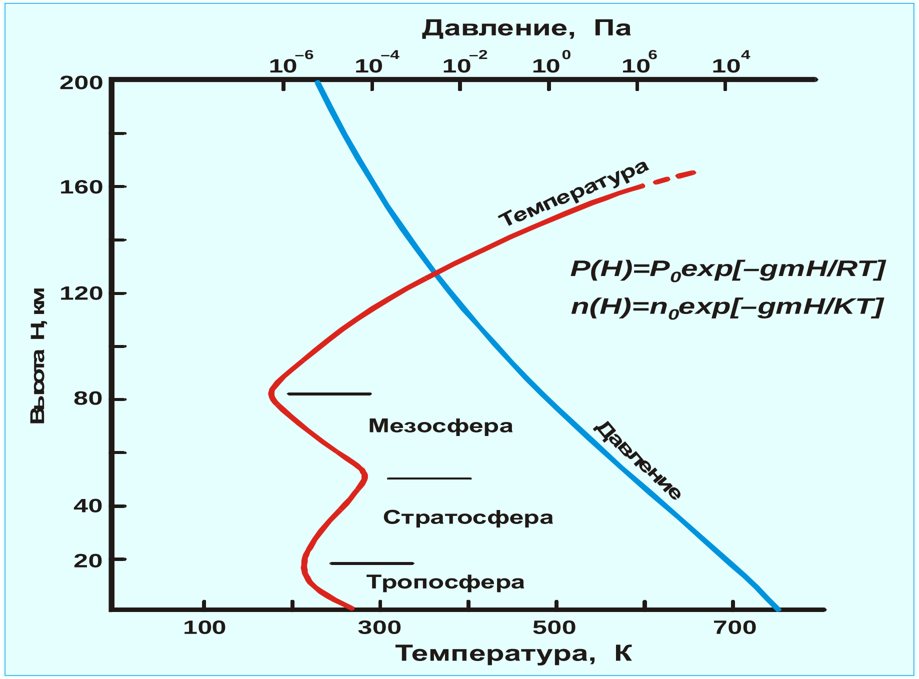
- Photochemical oxidation of SO2 in the air
- a)SO2 is activated by free radicals OH,HO2, etc.
- b) SO2 is activated by sunlight with SO2 exitation in **high electronic states of SO2** with energy > 2 Ev ( ~ 45 kcal/mole) **(exited SO2 reactions)**

## SO2exited + SO2 à SO3+SO is dominate?




## SO2+OH à H2SO4 is dominate

# Atmospheric structure




## Temperature and pressure vertical distribution

| Region | Range, km | pressure, Torr | Temperature, °C | |
|---|---|---|---|---|
| Stratosphere | 18 – 50 | | – 56 | – 2 |
| Troposphere | 0 –-18 | 760 -…. | 15 | – 56 |

# Heterogeneous oxidation of SO2 à H2SO4

$SO_2$ is absorbed by fly ash and soot particles.

**Photocatalysis is possible on metal oxides particles that have semiconducters properties** ($TiO_2$, ZnO,etc.)

$$MeO \xrightarrow{h\nu} (MeO^{+}, e^{-}) \xrightarrow{\hat{I}_2} (MeO^{+})(O_2^{-})_{Адс.} \longrightarrow 2(O^{\cdot})_{Адс.}(MeO)$$

$$(MeO^{+}, e^{-}) \xrightarrow{H_2O_2} (MeO^{+})(H_2O_2^{-})_{Адс.} \longrightarrow 2(HO^{\cdot})_{Адс.}(MeO)$$

$$2(O^{\cdot})_{Адс.}(MeO) \xrightarrow{SO_2} [SO_2(O^{\cdot})]_{Адс.}(MeO)(O^{\cdot}) \longrightarrow (SO_3)_{Адс.}(MeO)(O^{\cdot})$$

$$(SO_2)_{Адс.} + 2(HO^{\cdot})_{Адс.} \longrightarrow [SO_2(HO^{\cdot}{}_2)]_{Адс.} \longrightarrow (SO_4^{2-})_{Адс.} + 2(H^{+})_{Адс.}$$

# Chemical Ways of SO2 oxidation

- Reactions on soot and atmospheric particles ( **heterogenic oxidation**)
- Reactions in rains (**in liquid phase)**
- Reactions of photocatalysis by particles (ZnO )

- Photochemical oxidation of SO2 in the air
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# Homogeneous oxidation where $SO_2$ is " passive" reactant



| Reaction | k $cm^3/s$ | Oxidant concentration, $cm^{-3}$ | time, h. |
|---|---|---|---|
| $SO_2 + O_2 \rightarrow SO_3 + O^{\bullet}$ | $10^{-30}$ | $5 \cdot 10^{18}$ | 50000000 |
| $SO_2 + O_3 \rightarrow SO_3 + O_2$ | $10^{-22}$ | $8 \cdot 10^{11}$ | 3000000 |
| $SO_2 + HO^{\bullet}_2 \rightarrow SO_3 + HO^{\bullet}$ | $7{,}8 \cdot 10^{-16}$ | $3 \cdot 10^{8}$ | 1200 |
| $SO_2 + CH_3OO^{\bullet} \rightarrow SO_3 + CH_3O^{\bullet}$ | $1{,}8 \cdot 10^{-14}$ | $7 \cdot 10^{7}$ | 227 |
| $SO_2 + HO^{\bullet} + H_2O \rightarrow H_2SO_4 + HO^{\bullet}_2$ | $1{,}8 \cdot 10^{-12}$ | $1{,}8 \cdot 10^{6}$ | 86 |

**SO2 oxidation proceeds due to formation of secondary S radicals:**

$SO_2 + HO^{\bullet} \rightarrow HSO_3^{\bullet}$

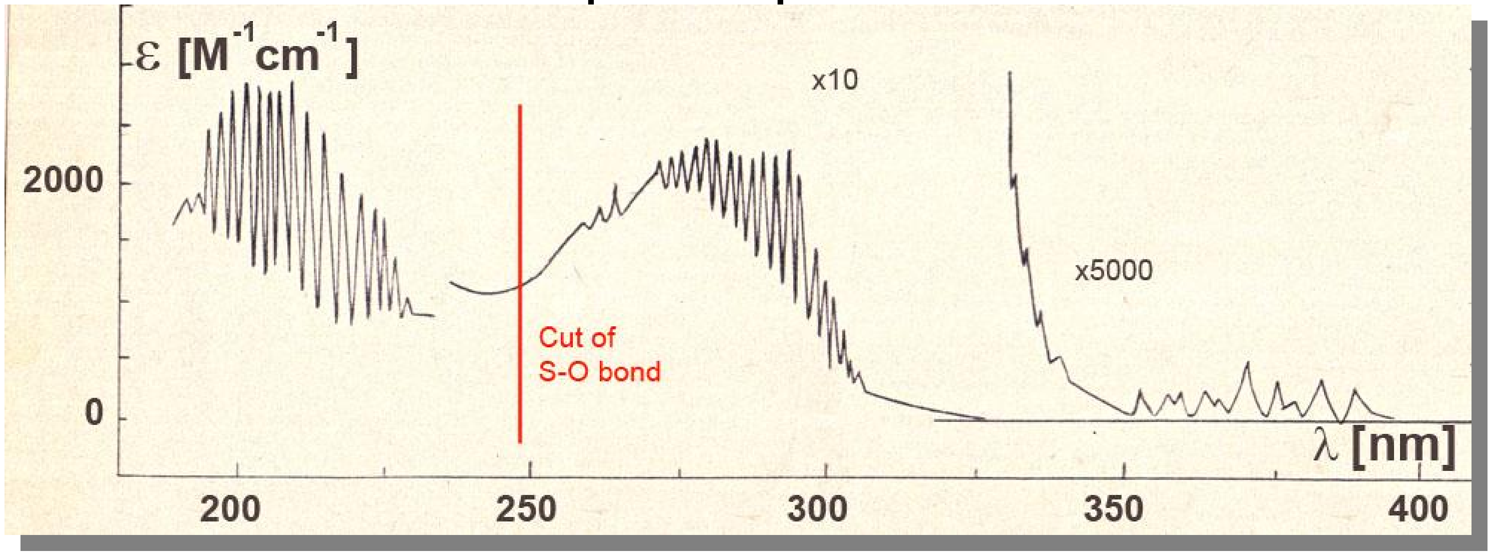
$HSO_3^{\bullet} + O_2 \rightarrow HSO_5^{\bullet}$

$HSO_3^{\bullet} + NO2 \rightarrow HSO_4^{\bullet} + NO$

$HSO_4^{\bullet} + NO_2 + H_2O \rightarrow H_2SO_4 + HNO_3$

# SO2 can be photoactive reactant in the atmosphere

Absorption spectra of SO2



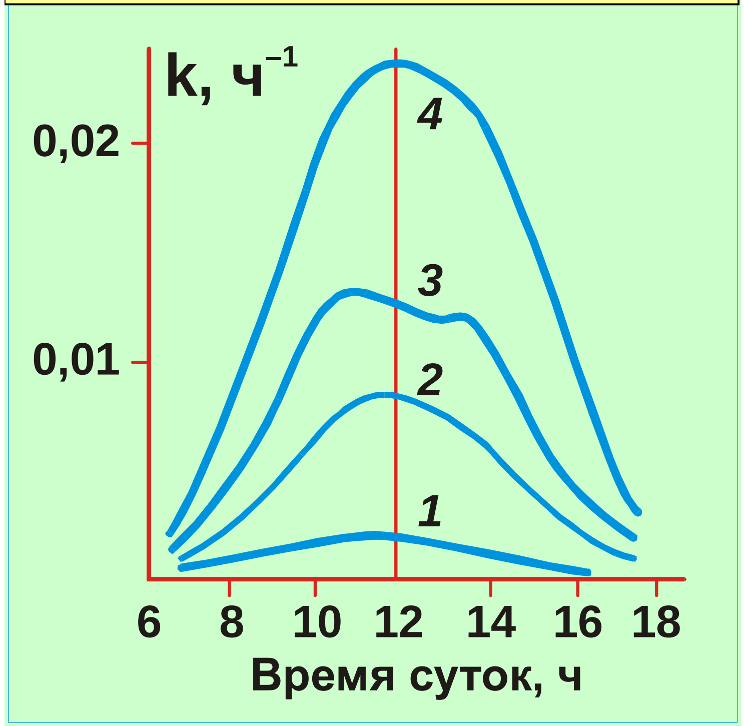

| | | |
|---|---|---|
| $^3SO_2 + SO_2 \rightarrow$ | 330-390nm | very week band $^3B_1$ ; E~25-50 kcal |
| $^{1,3}SO_2$ + SO2 $\rightarrow$ | 260-340 nm | week bands $^1B_1$, $^1A_2$ ;E ~ 50-90 kcal |
| Energy D (OS-O) = 5эB=247 nm | 1800-2400A | Strong band, OS-O à O + SO ; 247nm |

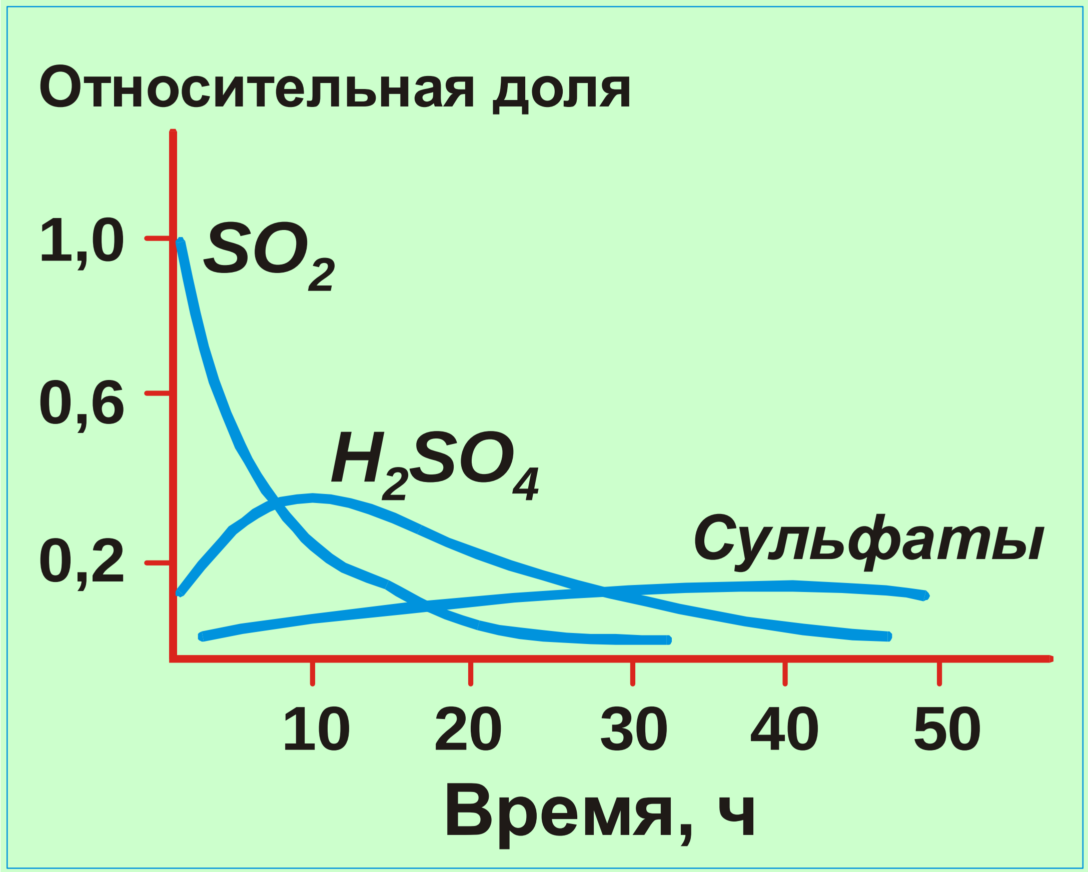
# Heterogeneus oxidation of $SO_2$



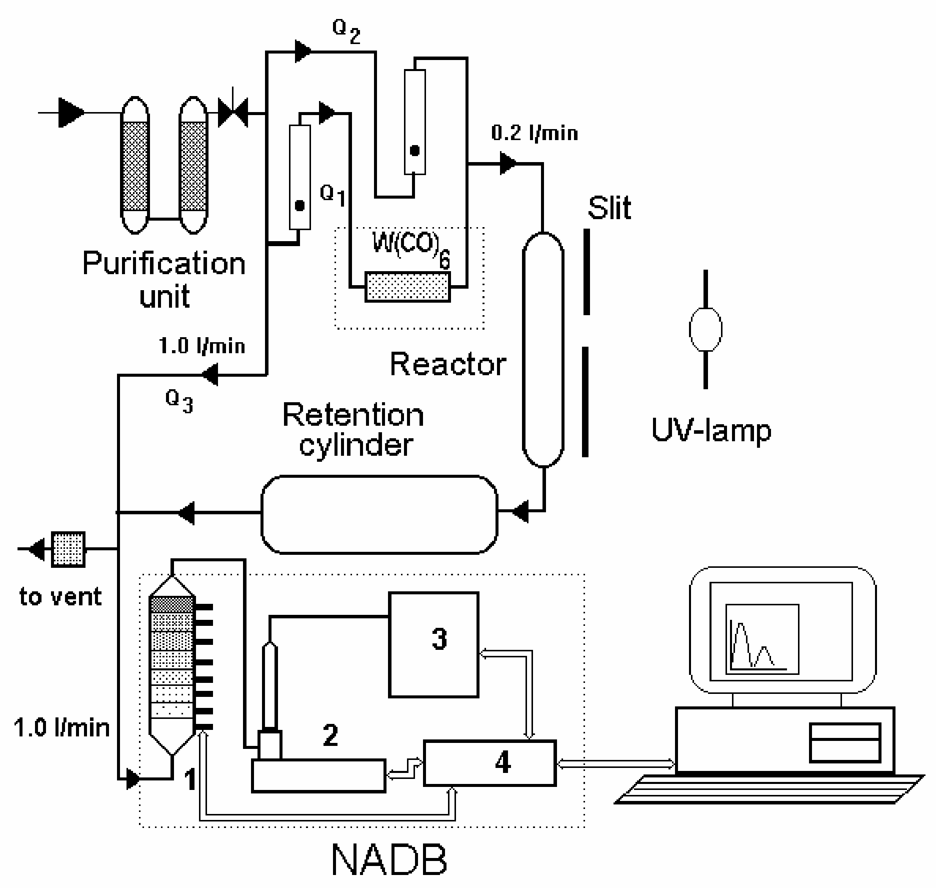
Soil and dust particles absorb SO2 and O2 and catalyze transformation SO2 à H2SO4

Dependence of Rate of SO2 oxidation over power plants



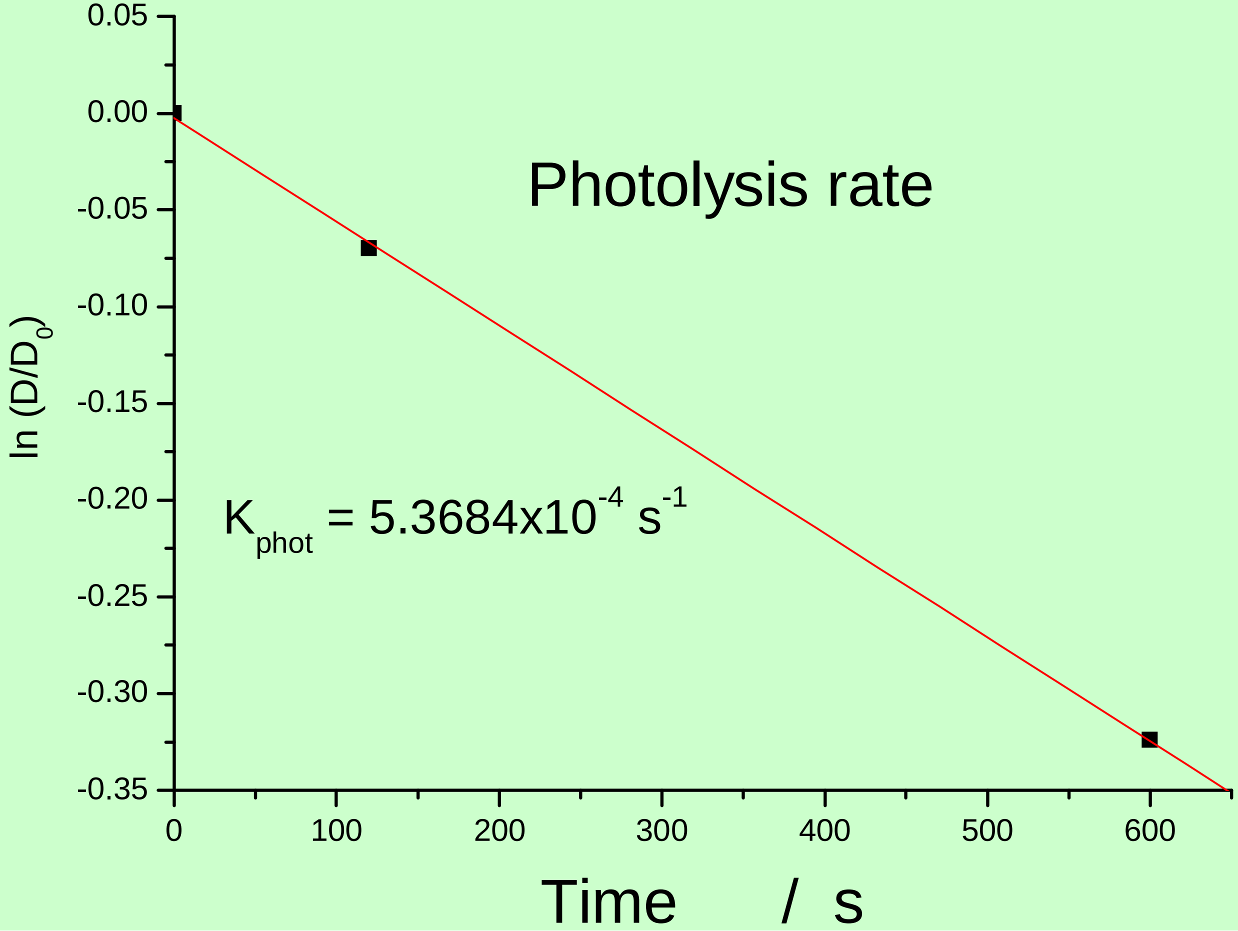



- Experimental set-up for study of photonucleation

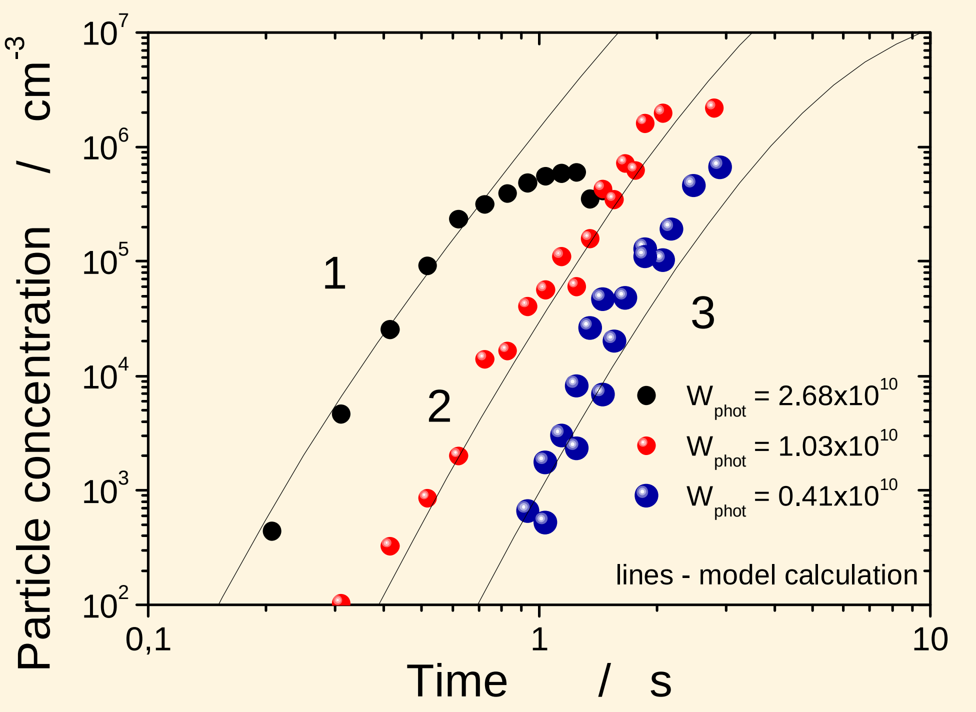


- Kinetics of Photolysis of gas precursor of aerosol formation





# Grows of particles in time during UV action on precursor vapor in gas phase




**Rate of birth of particles**
**=**
**Rate of photolysis of precursor in the gas phase**

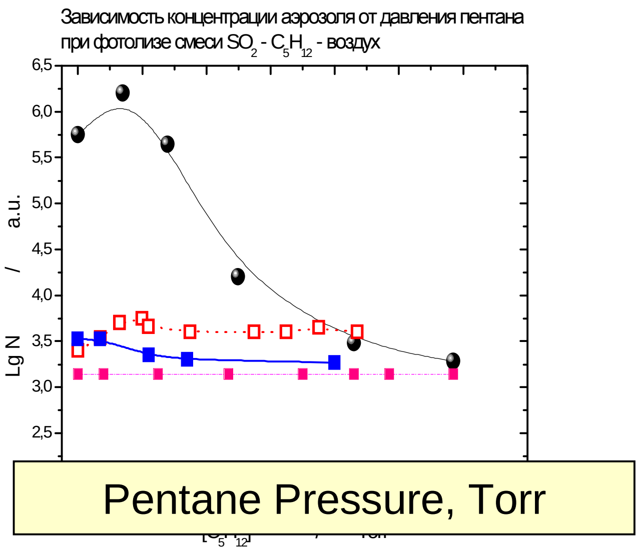
**Comparison of modeling and experimental data allows to calculate key value of the photonucleation - rate of birth of particles**

# SO2 photonucleation is dependent on n-pentane pressure

in SO2+C5H12+air mixture for reaction

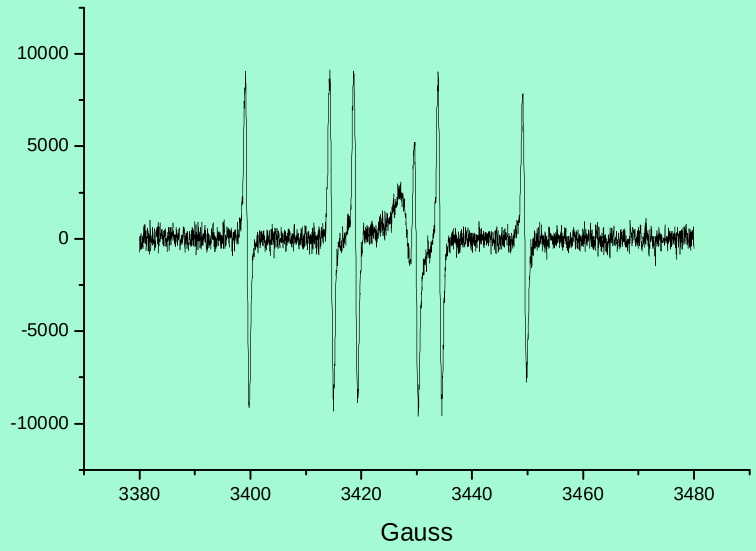
**NOTE**: Photoaerosol of **HRSOx acids** **continue to grow in dark**

**but** photoaerosol of **H2SO4 does not grow in dark**



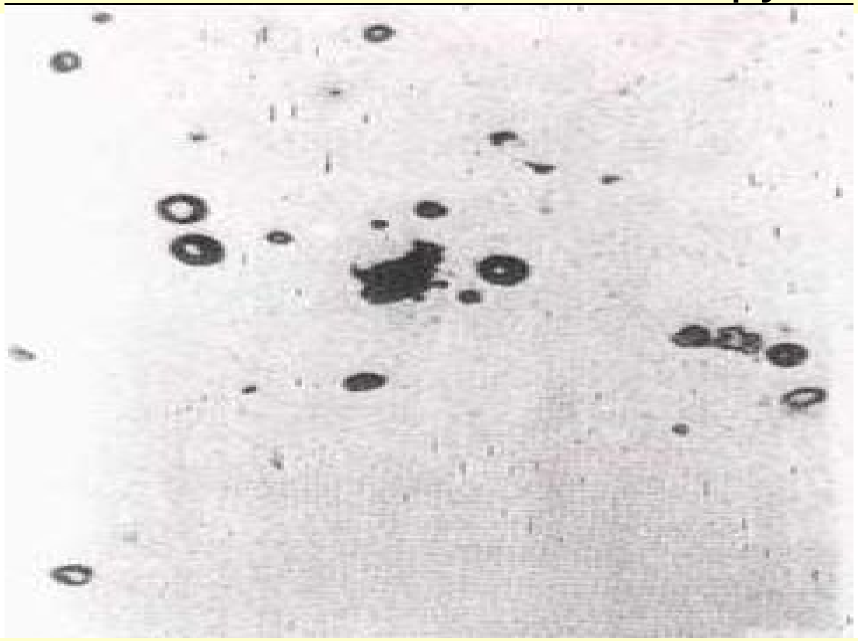
# Application HPLC, ESR, NMR,UV,IR,MS methods for analysis of chemical properties of photoproducts

Detection of short-lived radicals OH by spin traps ESR method




Dultseva, G.G., Skubnevskaya, G.I., Volodarsky, L.V.,Tikhonov, A.Y. *J.Phys.Chem.* 1996**,** *v.100, 17523*

Analysis of Sulphate aerosol by Bigg's method with electron microscopy help



Mironenko V.E., Graduate work, NSU (1982)

# Analysis of gas and aerosols products

*Methods and approach for particles analysis employed*

- **Procedures of sample preparation , arte-facts elimination**
- **High Performance Liquid Chromatography**
- **UV, IR spectroscopy**
- **NMR spectroscopy**
- **Electron microscopy**
- **Gas chromatography – Mass spectrometry**
- **Thin Layer Chromatography**
- **Qualitative analytical procedures for functional groups**
- **Ion chromatography**
- **Etc.**

# Chemical analysis of gas and aerosols



*Basic methods and approach for particles analysis*

- **High Performance Liquid Chromatography**
- **UV, IR spectroscopy**
- **NMR spectroscopy**
- **Electron microscopy**
- **Gas chromatography – Mass spectrometry**
- **Thin Layer Chromatography**
- **Qualitative analytical procedures for functional groups**
- **Ion chromatography**

# What kinds of Gas Photochemistry are possible to lead to new nanoparticles generation in Earth atmosphere??????

Primary sunlight action hv produces short living active intermediates R i : hv+M " Mi; R1 + R2 " **GAS** products

MAJOR WAY

?????

R1,R2 +Mj " Ri + M nano**particleS**

**<u>MINOR WAY</u>**

???????

R or not R participate–***what is the question***

# Numerical modeling of Photonucleation



*Basic model and further approach*

**-Basic Model of nucleation witn fixed source of embryos is applied (Mc Murry etc).**

*Smoluchowsky model+ fixed source for further growth of particles.*

- ***improved model by Koutsenogy K.P.,Levykin A., Dubtsov S,etc.(1982-2005)***

***Siberian approach***

**-Application of McMurry model to photonucleation.**

**steady source of embryos is activated by sunlight ONLY**

**- More effective algorithm for numerical modeling is prepared**

**- Experimental data of photonucleation is modeling with most accuracy.**

- **Due to comparing experimental data with numerical modelong**
- **Rate of the initiall step of photonucleation is calculated at the first**

``````````````````````
``````````````````````

# CONCLUSIONS

***New properties of phenomenon:***

- Formation of particles is result of UV light action ONLY
- Specific photochemistry of gas precursor of particles is very important
- Composition of all gas mixtures affects on photoaerosol yield strongly First
- Dose of illumination of precursor limits photoaerosol yield Modification of time or intensity of light action brings the same concentration of new Sparticles

**Specific Aerosol formation under UV light action –fundamental results**

# The application of $SO_2$ studies for environmental problems



- Monitoring of air quality and acidity of rains in region of Bailkal lake ($O_3$,$SO_2$, $NO_x$,aerosols, pH precipitaions etc)

Acid rains pH <~ 4 (!) can be explained by $SO_2$ photochemical transformation into $H_2SO_4$ partially

- We expertized the air quality ( 1987-2005) of Novosibirsk region, Tomsk ,Kemerovo, Novokuznetsk – West Siberian Cities
- We monitored Novosibirsk Power plants wastes on contents of $SO_2$,$O_3$, $NO_x$, HCHO, aerosols, acidity of precipitations., etc. at the distances up to 90 km from Novosibirsk ( *in collaboration with Belan B and .,Panchenko M. team,IOA SB RAS)*
- Laboratory modeling of photosmog with UV light+$SO_2$ + pentane+ air mixture in small aerosol camera of IOA, Tomsk, 1982 ( Zuev V.E, Ippolitov I. I ,Kozlov V. and IOA team)
- Participation in Novosibirsk Scientific Ecological Program of NSC (1990-1994*)* headed by acad. Koptyg V.A.
- *Environmental Department of Novosibirsk expert opinion of air quality of Novosibirsk region*

-

# Participation of colleagues in SO2 Project realization (1981-2005)

| | |
|---|---|
| **Sut-up , methods of analysis** | **А.Н.Анкилов, С.Н.Дубцов, Г.Г.Дульцева, Е.Н.Дульцев** |
| **Monitoring in Siberian region** | **А.Н.Анкилов, С.Н.Дубцов, А.М.Бакланов, А.Н.Козлов, Г.Г.Дульцева, Е.Н.Дульцев** |
| **Photonucleation in lab** | **С.Н.Дубцов, А.Н.Анкилов, Е.Н.Дульцев** |
| **Identification of gas and aerosol products** | **Г.Г.Дульцева , Мироненко В. , Пащенко С.Э.** |
| **Numerical modeling** | **В.В.Пененко, Алоян А.Е., Н.М.Бажин, А.В.Кейко, А.И.Левыкин, Куценогий К. П** |

# Some basic publications

Скубневская Г.И., Бажин Н.М., *Метеорология и гидрология,* 1982, № 9, С. 113-124

Пененко Скубневская Г. И., *Успехи химии* 1990

Скубневская Г И Дульцева Г Г Дубцов С Н Дульцев Е Н, *Химия устойчивого развития,* 1999

**Skubnevskaya G.I., Dubtsov S.N., Dultsev E.N., Dultseva G.G. and Wing Tsang J.Phys.Chem 2004, August**

.

. *Пененко В.В.,Бажин Н.М.,Бобылева И.М.Цветова Е А Скубневская ГиИ Метеорология и гидрология 1989 №7 С.76-84.*

# Sponsor supports of team:

**Grants of SB RAS «Siberian Aerosols» и «Siberian Cities Ecology»(1990-2004)**

**RFBR Grants (1992-2004)**

**Budget of Government support since 1980**

**USA-Russian Grant CRDF (2002-2003)**

# What can be news in future XXI for photonucleation of $SO_2$ studies and applications for Earth sciences?

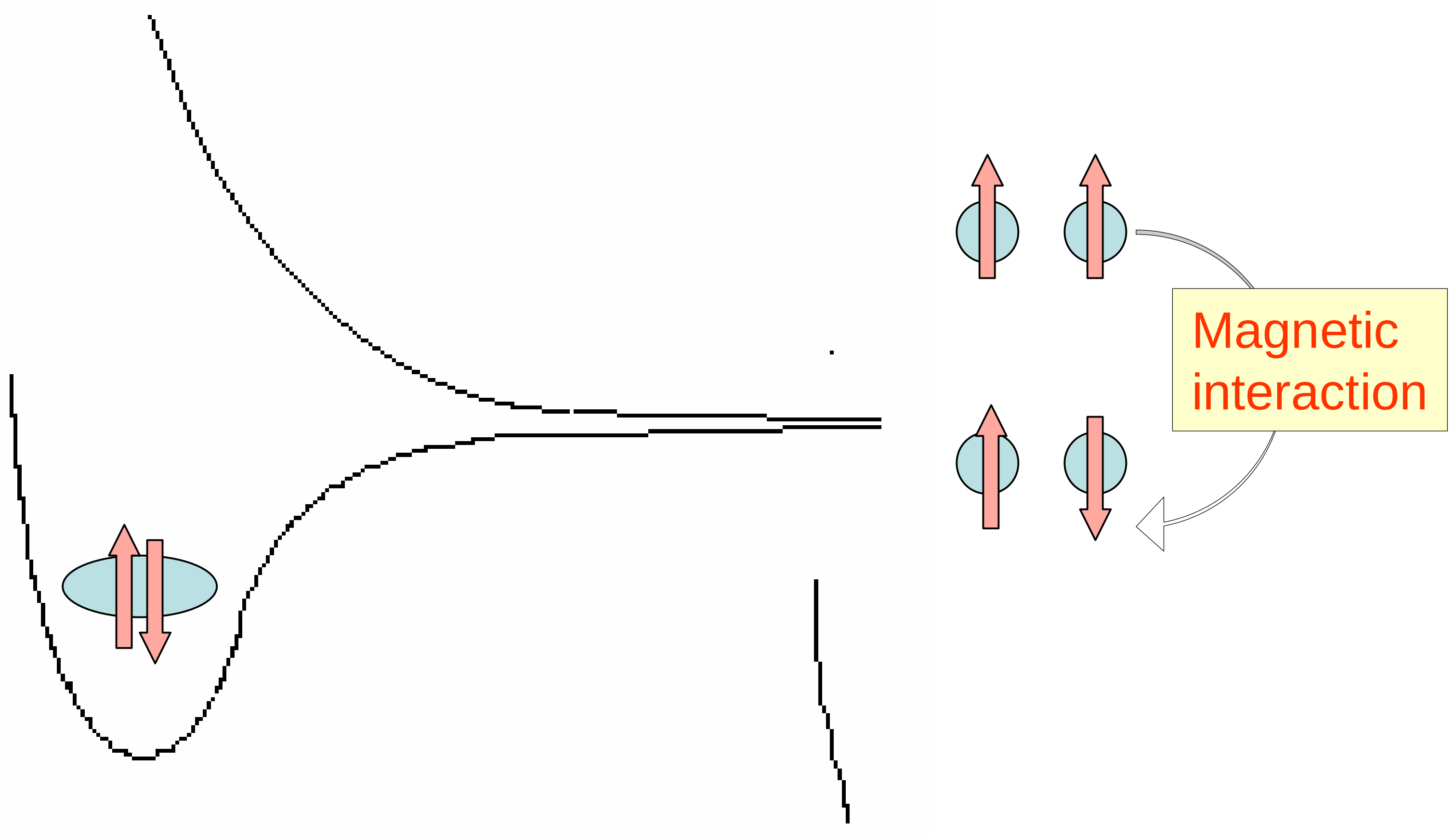
- Is it possible to find the influence of magnetic field of the Earth on the nucleation of $SO_2$ under sunlight action? *( our preliminarily results-* *YES)*

- *What will magnetic field studies of photonucleation can help in future ??*

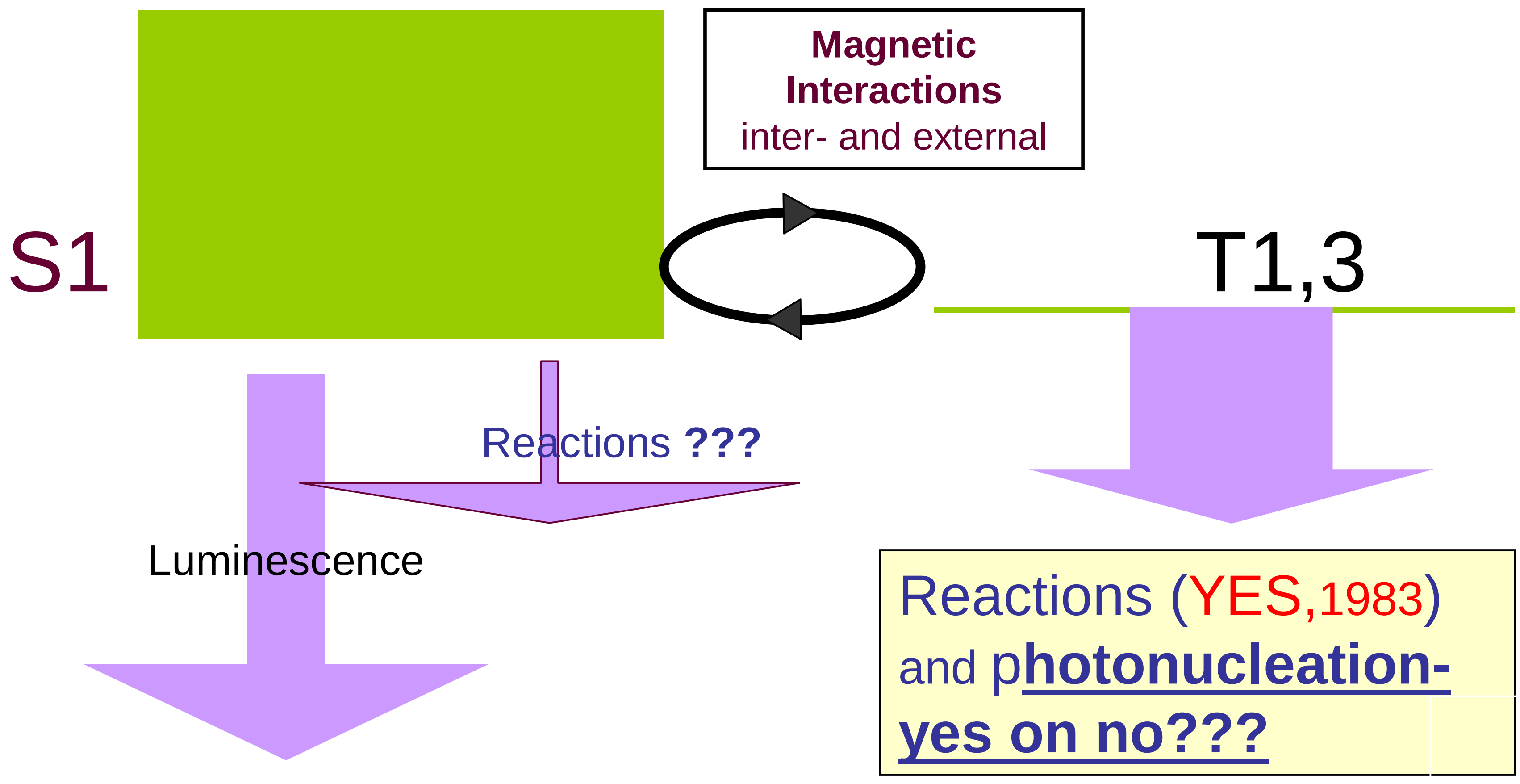
Getting inside spin chemistry of sunlight exited $SO_2$ states in Earth atmosphere and understanding generation of sulphate aerosol layer (Junge layer h~16-18 km).Aerosol layer is situated situated under ozone layer.

It wiil become possible to explain changing intensity of rains in different regions of Earth due to Earth magnetic field and magnetic storms of Sun variations that cause Junge sulphate aerosol layer variations under these magnetic impetus to rains flow .

**Spin chemistry** of SO2 exited by sunlight
Not Energy,BUT **selection of reaction ways by Earth maghetic field**
(as energy train is ruled by railway  operator)



# Chemical transformation $SO_2$ is regulated by **S**inglet and **T**riplet states oscillation of exited $SO_2$



# Thank you for your attention

*Our Institute, Novosibirsk, 2005*