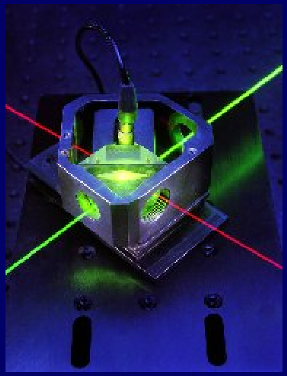
Laboratory for Atomic, Molecular and Laser Spectroscopy

Practical Expirience with Photoacoustic Spectroscopy: Air Monitoring



Dr. Dragan D. MARKUSHEV

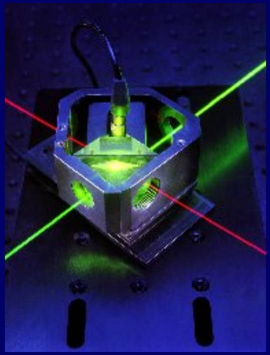
Institute of Physics

11080 Beograd – Zemun, SERBIA

International Summer School 5.-18. June 2011, Nova Gorica, Slovenia

Air Monitoring by Photoacoustic Spectroscopy

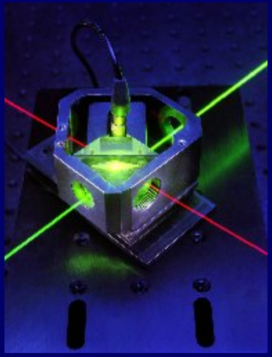
- In recent times the atmospheric pollution has become an issue of a great concern. Well-known phenomena such as a green house effect, acid rain, photochemical smog formation, stratospheric ozone depletion etc. are strongly related to the increasing of trace species. Growing human activities are increasing atmospheric concentrations of carbon dioxide (CO_2) and other, so called “trace gases”, that are leading to changes in the fundamental chemical and physical composition of Earth's atmosphere.



Introduction

Air Monitoring by Photoacoustic Spectroscopy

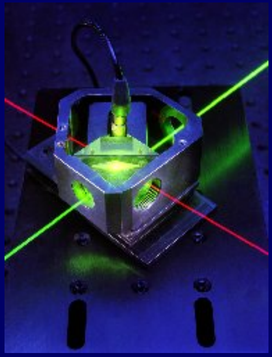
- It has been recognized that even trace concentrations of some atmospheric species can have a substantial impact in diverse areas. Beside the well known CO_2, CO, NH_3, NO_x, SO_2, C_2H_4, CH_4, O_3, CFCs, HFCs, PFCs, special concern must be given to some specific trace gases with purely anthropogenic origins such as a sulfur hexafluoride (SF_6) and SF_6 – like molecules (for example trifluoromethyl sulfur pentafluoride – SF_5CF_3), known as a strong absorbers in the thermal infrared window region and as a molecules with long atmospheric life time and high global warming potentials.



Introduction

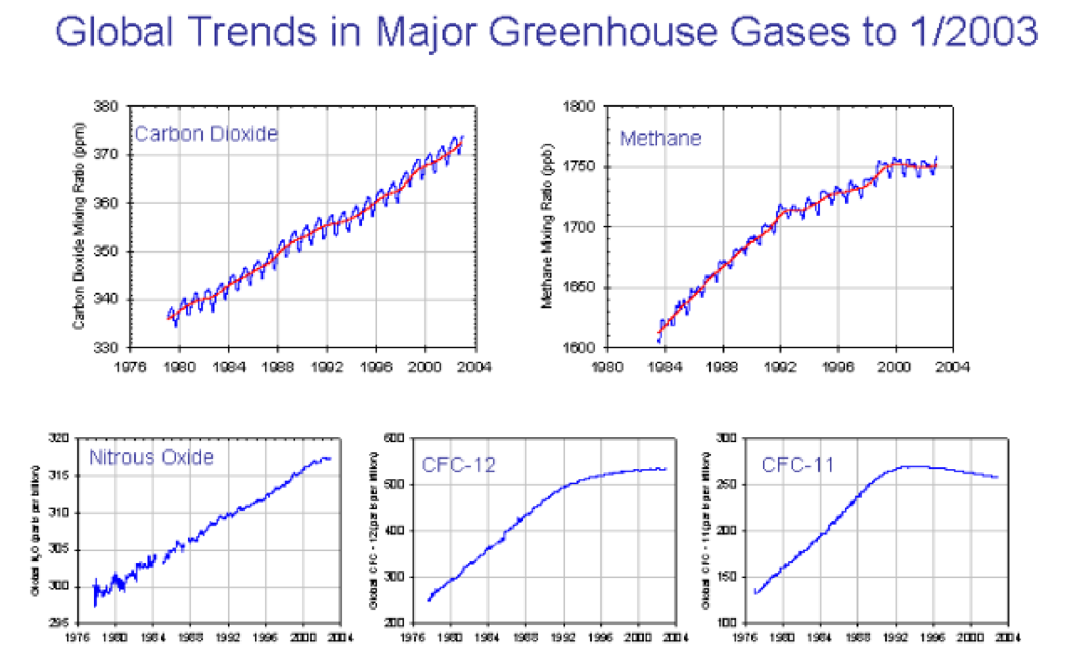
Air Monitoring by Photoacoustic Spectroscopy

CFC's and Miscellaneous Gases	Pre-industrial baseline	Natural additions	Anthropogenic additions in ppbv	Present tropospheric concentrations	GWP
CFC-11 (trichlorofluoromethane) (CCl_3F)	0.000000	0.000000	0.262000	0.262000	1320
CFC-12 (dichlorodifluoromethane) (CF_2Cl_2)	0.000000	0.000000	0.533000	0.533000	6650
CFC-113 (trichlorotrifluoroethane) ($C_2F_3Cl_3$)	0.000000	0.000000	0.083000	0.083000	9300
HCFC-22 (chlorodifluoromethane) ($CHClF_2$)	0.000000	0.000000	0.118000	0.118000	1350
sulphur hexafluoride (SF_6)	0.000000	0.000000	0.003500	0.003500	23,900
trifluoromethyl sulphur pentafluoride (SF_5CF_3)	0.000000	0.000000	0.000120	0.000120	20,000
perfluoroethane (C_2F_6)	0.000000	0.000000	0.004000	0.004000	9200

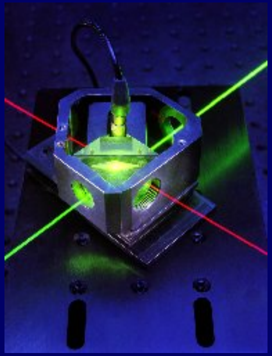


Recent Atmospheric Concentrations

Air Monitoring by Photoacoustic Spectroscopy



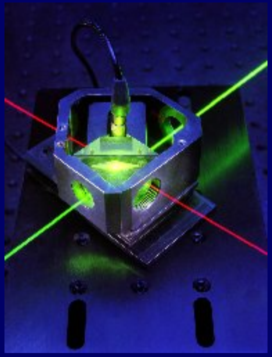
Global trends in major long-lived greenhouse gases through the year 2002. These five gases account for about 97% of the direct climate forcing by long-lived greenhouse gas increases since 1750. The remaining 3% is contributed by an assortment of 10 minor halogen gases, mainly HCFC-22, CFC-113 and CCl_4.



Recent Atmospheric Concentrations

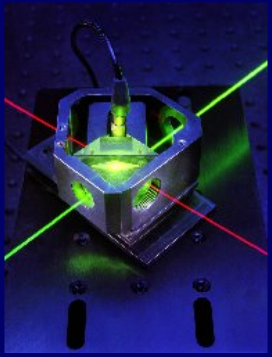
Air Monitoring by Photoacoustic Spectroscopy

	CO_2	SF_6
Pre-industrial concentration	280 ppm	0
Recent Atmospheric concentration	~380 ppm	~5 ppt
Atmospheric lifetime (years)	50-200	3200
GWP	1	~24000



Air Monitoring by Photoacoustic Spectroscopy

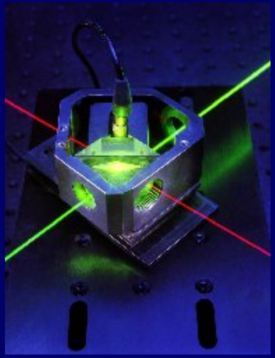
- In the past, numerous techniques have been developed and successfully applied to the trace gas monitoring. One of them is infrared photoacoustics spectroscopy (PAS), which is used not only for precise detection and measurements of minimal trace gas concentrations in the atmosphere (minimum and maximum concentrations extend into the parts-per-trillion to percent ranges) but for their intensive investigation on atmospheric and subatmospheric pressures trying to reach the through understanding of complex physical and chemical processes and interactions involved.



Photoacoustic Spectroscopy In General

Air Monitoring by Photoacoustic Spectroscopy

- The photoacoustic spectroscopy is based on the sensitive detection of acoustic waves launched by the absorption of pulsed or modulated laser radiation via the transient localized heating and expansion in an investigated gas sample. This effect is caused by the transformation of at least part of the excitation energy into kinetic (translational) energy through the, so called, energy exchange processes induced by mutual collisions of irradiated species.

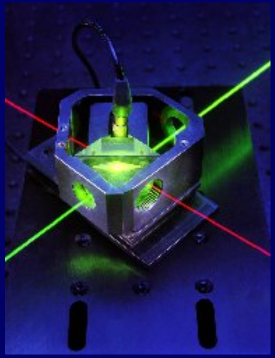


Photoacoustic Spectroscopy Fundamental

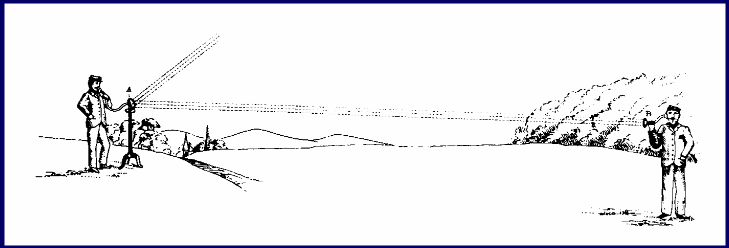
Air Monitoring by Photoacoustic Spectroscopy

- Observed first by Bell in 1880.
- Method of PAS was formally introduced in 1973.

Alexander Graham Bell

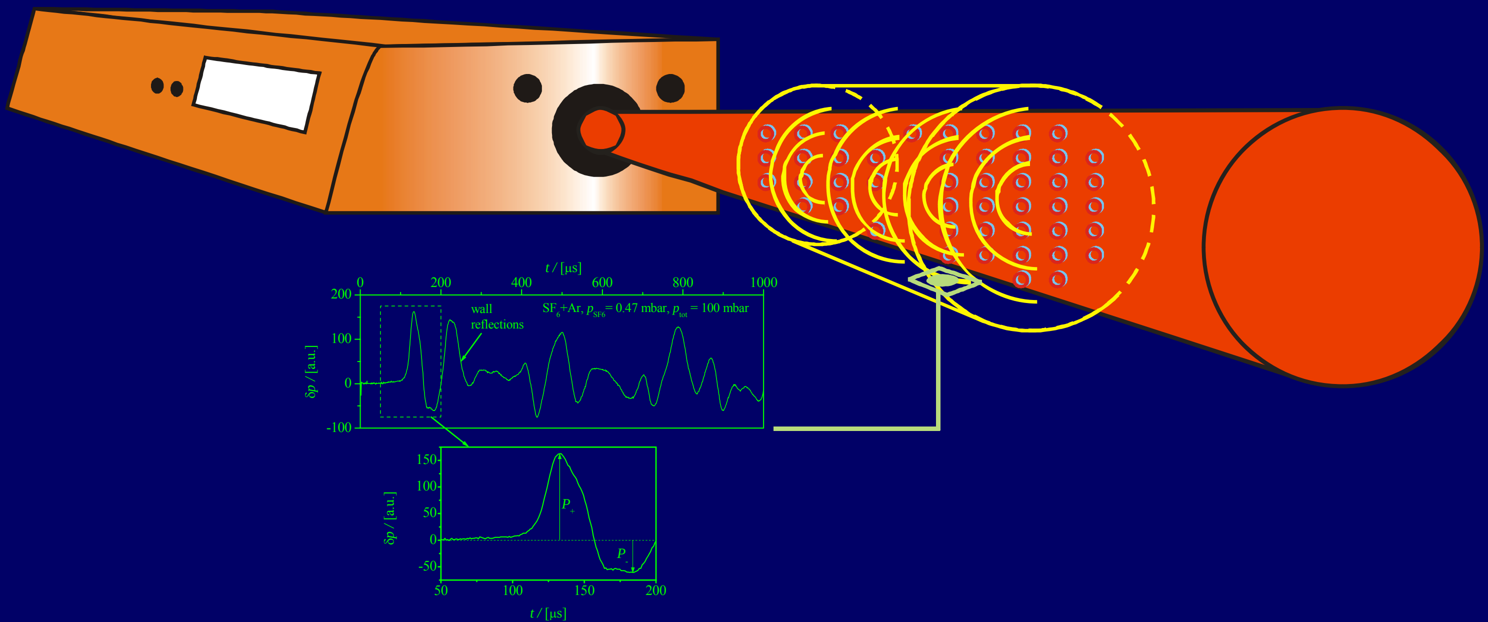


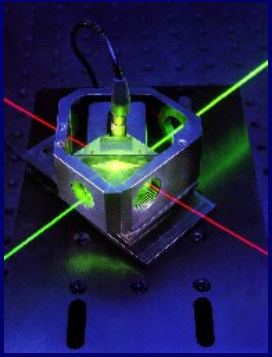
McPherson Photoacoustic Spectrometer



Historical background

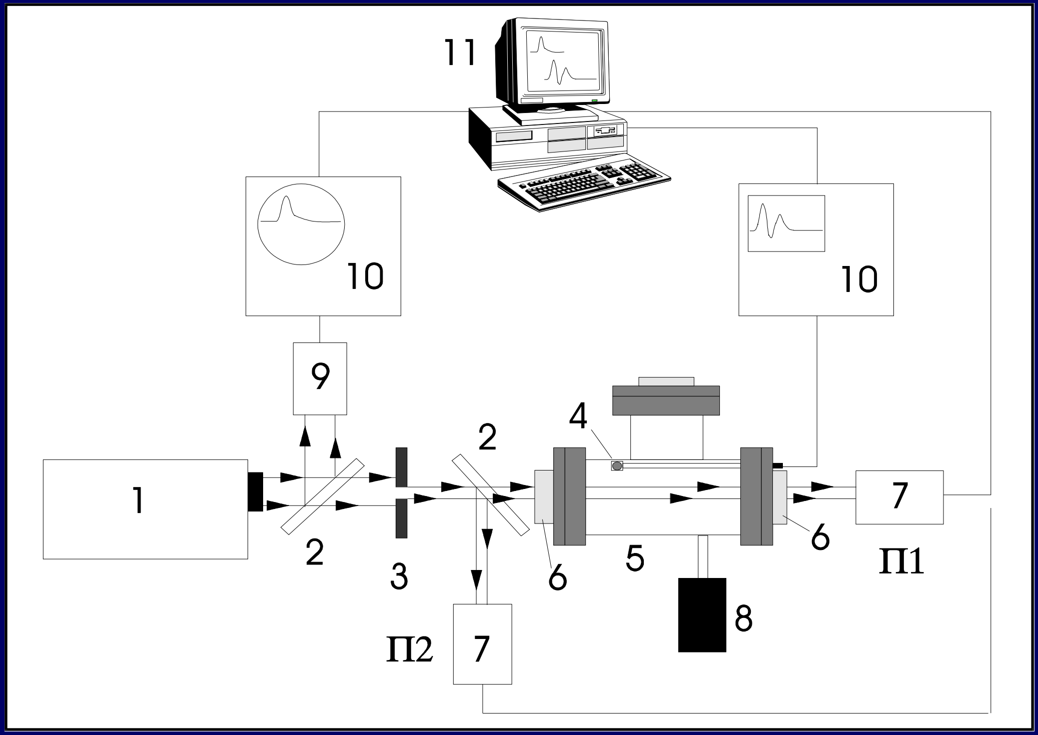
Air Monitoring by Photoacoustic Spectroscopy

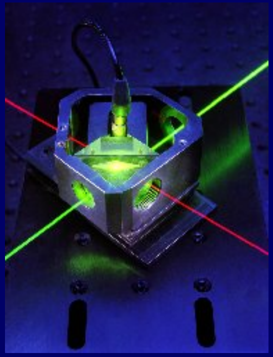




Experimental Set-up

Air Monitoring by Photoacoustic Spectroscopy



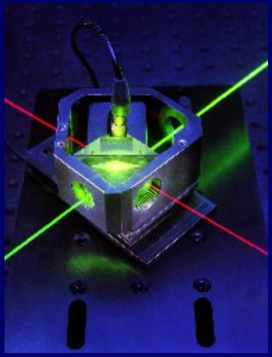


Experimental Set-up

Air Monitoring by Photoacoustic Spectroscopy

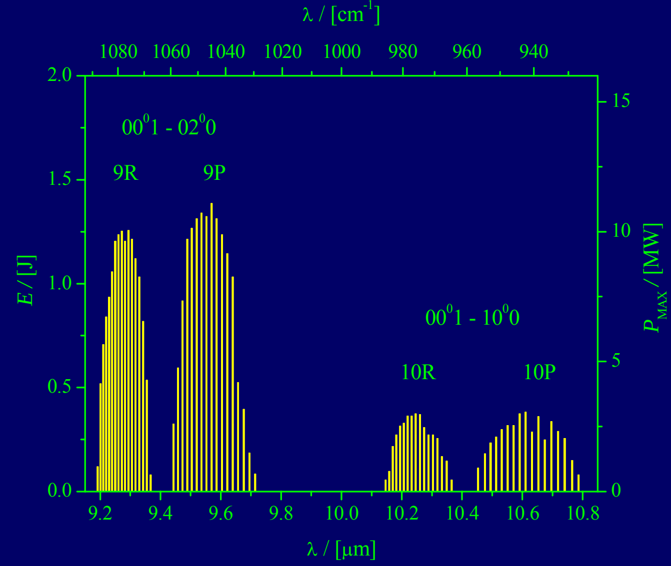
Ideally a detection technique (photoacoustics in our case), should fulfill the following requirements:

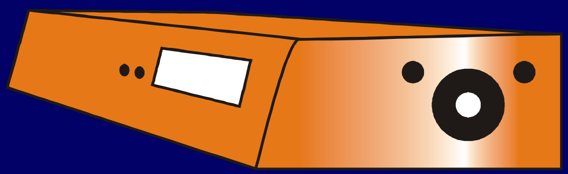
- a) feasibility of detecting numerous compounds with one instrument;
- b) high sensitivity in order to permit the detection of very low concentrations;
- c) high selectivity in order to differentiate between different species present in a multicomponent mixture;
- d) large dynamic range in order to monitor low and high concentrations with a single instrument;
- e) good temporal resolution to enable on-line monitoring;
- f) good portability for in situ measurements.

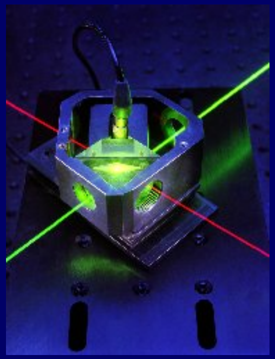


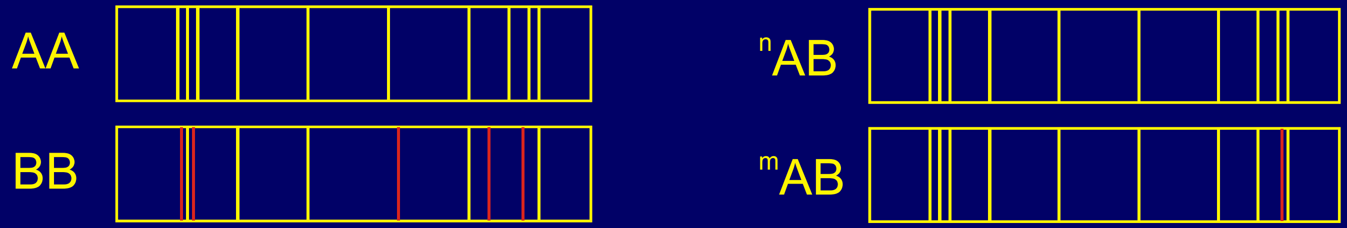
Photoacoustic Spectroscopy Requirements

Air Monitoring by Photoacoustic Spectroscopy



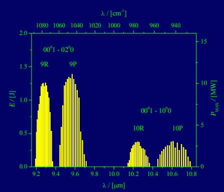






feasibility of detecting numerous compounds with one instrument

Air Monitoring by Photoacoustic Spectroscopy

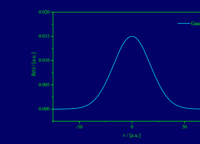


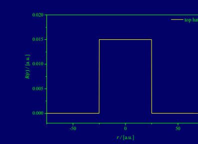
Energy

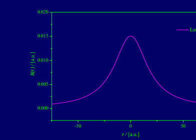
Operating mode

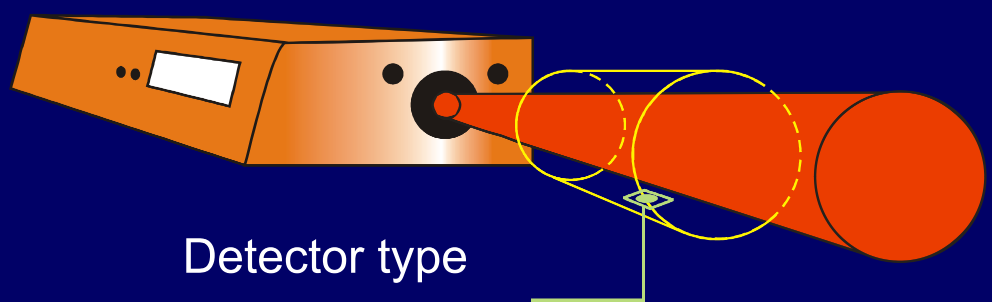
Continual or pulsed

Spatial and temporal characteristics

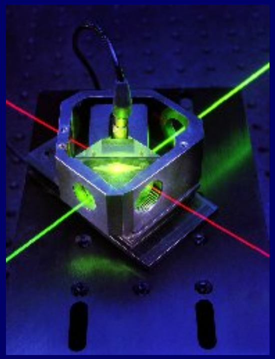


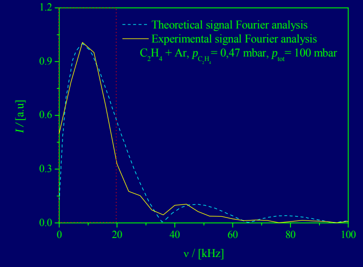




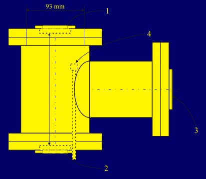


Detector type



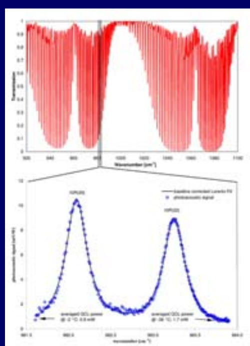


Geometry & Dimensions



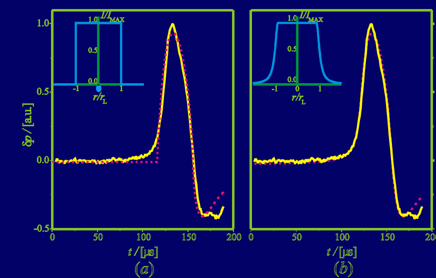
high sensitivity in order to permit the detection of very low concentrations

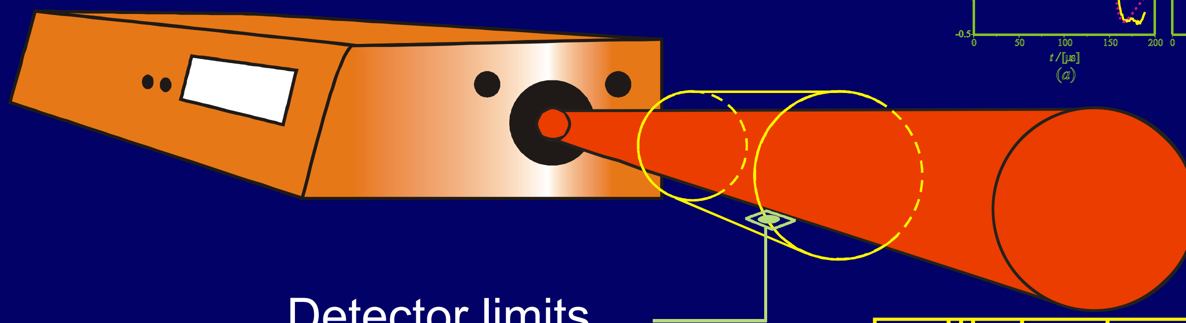
Air Monitoring by Photoacoustic Spectroscopy



Line width

Spatial and temporal characteristics



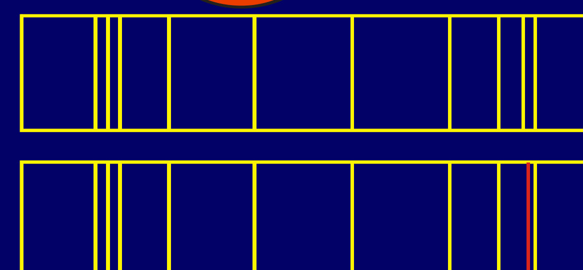


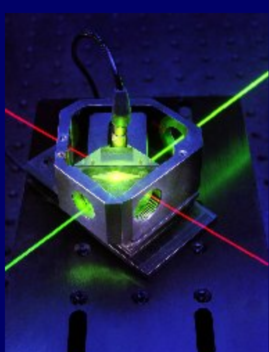
Detector limits

Capacitive microphones or other types

^{n}AB

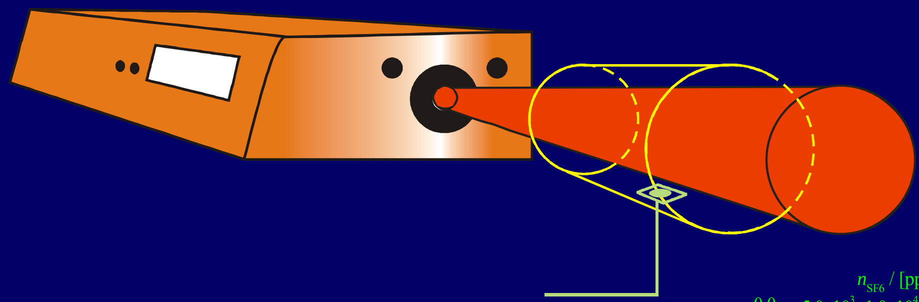
^{m}AB

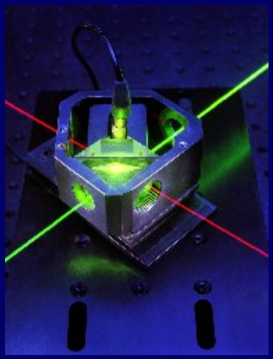


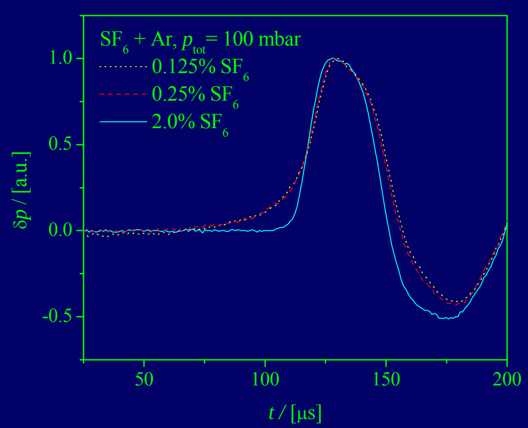


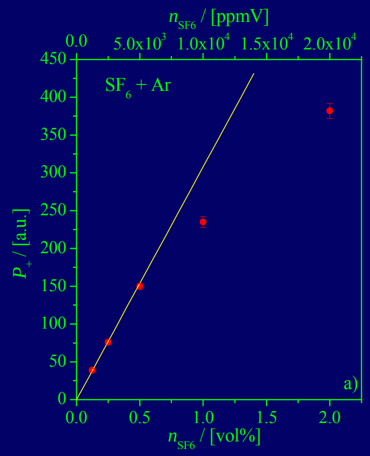
high selectivity in order to differentiate between different species present in a multicomponent mixture

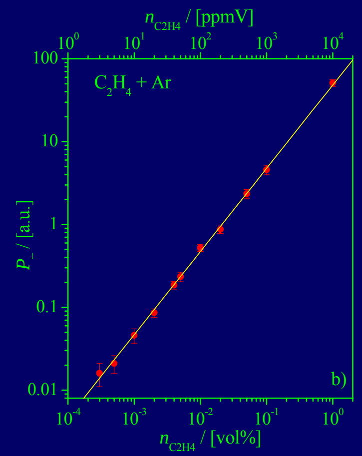
Air Monitoring by Photoacoustic Spectroscopy







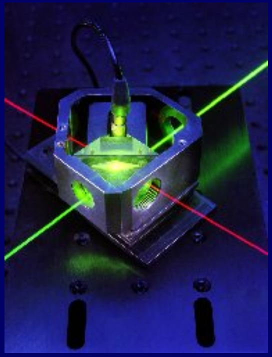


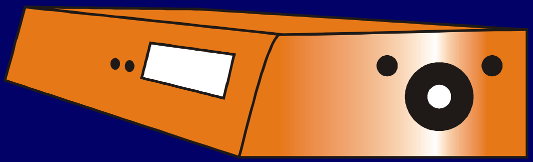


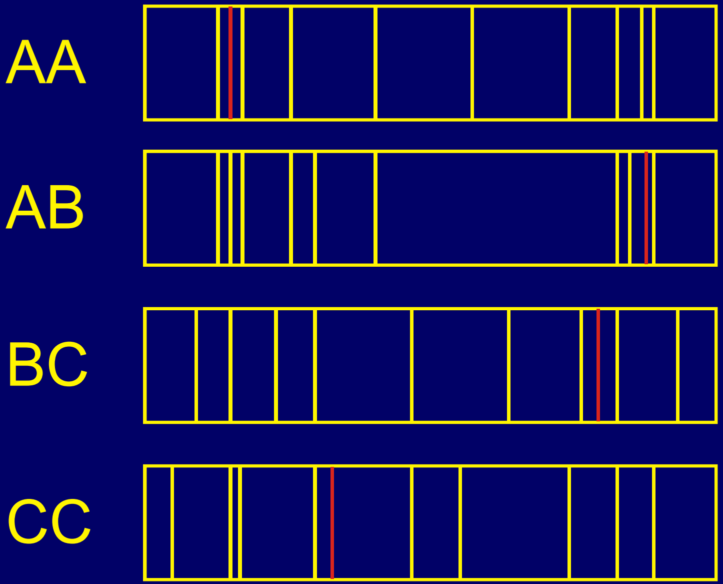
large dynamic range in order to monitor low and high concentrations with a single instrument

Air Monitoring by Photoacoustic Spectroscopy

Switching the wavelength in a reasonable time period for a different species detection



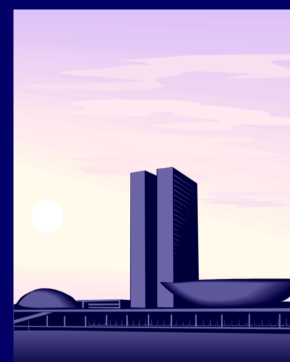


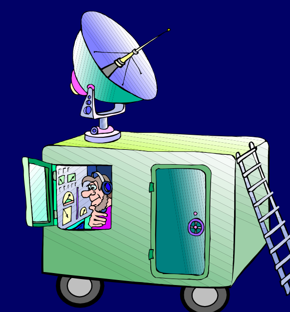
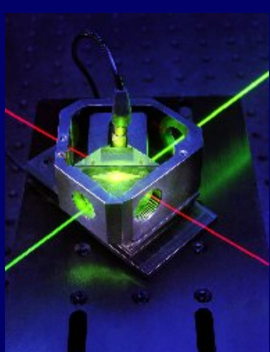
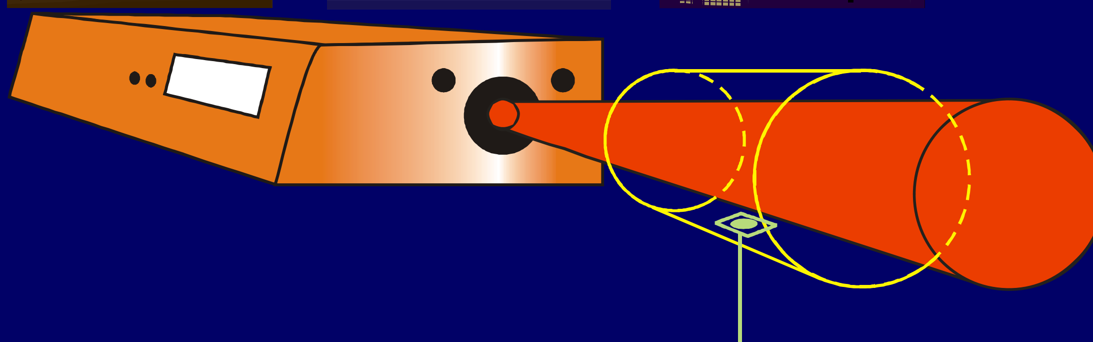
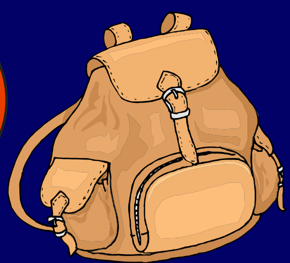


good temporal resolution to enable on-line monitoring

Air Monitoring by Photoacoustic Spectroscopy





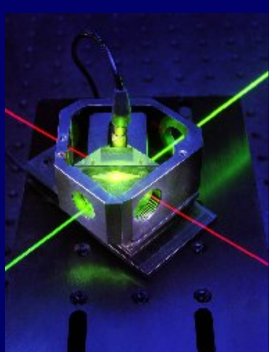
good portability for in situ measurements

Air Monitoring by Photoacoustic Spectroscopy

Generally speaking, air sampling can be performed by:

- a) extractive methods, based on the collection of air samples by an appropriate container and subsequent analysis;
- b) in situ monitoring methods offer the great advantage of real time measurements;
- c) remote sensing methods when the analyzer is located far away from the air sample under study.

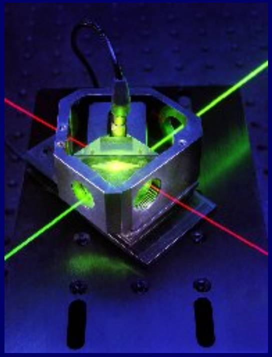
Photoacoustic spectroscopy is trying to find a compromise between extractive and in situ shemes



Photoacoustic Spectroscopy Air Sampling Methods

Air Monitoring by Photoacoustic Spectroscopy

The real progress in a photoacoustic spectroscopy (PAS) was connected to the progress made mainly in the fields of lasers and electronics. Using lasers as a radiation source, two major cases of irradiated sample excitation must be distinguished within the frame of this technique:



- *modulated* and *pulsed* depending of the laser operating mode;
- *linear* and *nonlinear* depending of the laser energy

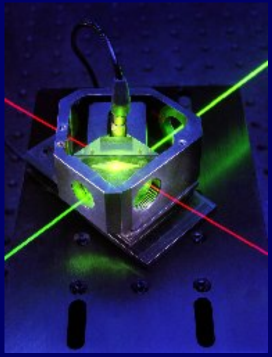
For our further discussion *pulsed* and *nonlinear* excitation will be considered.

Photoacoustic Spectroscopy and Sample Excitation

Air Monitoring by Photoacoustic Spectroscopy

Why pulsed excitation?

- No need for resonant cells
- No need for special geometry
- Calculation of the acoustic signals is simplified.
- Suitable for monitoring the collisionally induced processes at atmospheric and subatmospheric pressures
- Lower sensitivity limited by the cell geometry and microphone characteristics (frequency bandwidth)

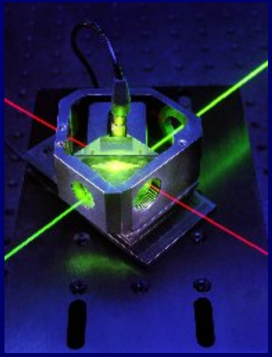


Photoacoustic Spectroscopy and Sample Excitation

Air Monitoring by Photoacoustic Spectroscopy

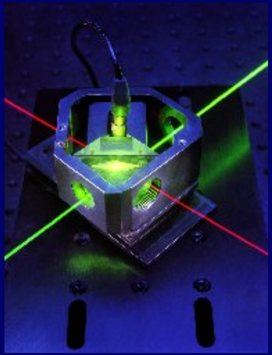
Why nonlinear excitation?

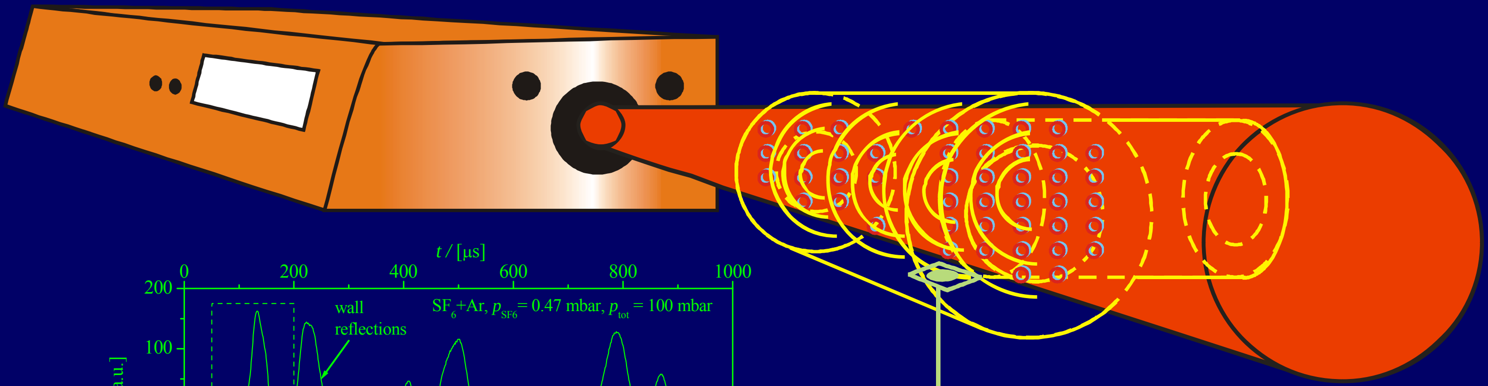
- Higher energies leads to higher absorption levels
- Higher absorption leads to efficient nonradiative relaxation
- Efficient nonradiative relaxation leads to better defined acoustic signals
- Better defined acoustic signals leads to higher sensitivity
- Suitable for monitoring the collisionally induced processes at atmospheric and subatmospheric pressures
- Nonwanted nonlinearity could lead to misunderstanding of the analyzed processes

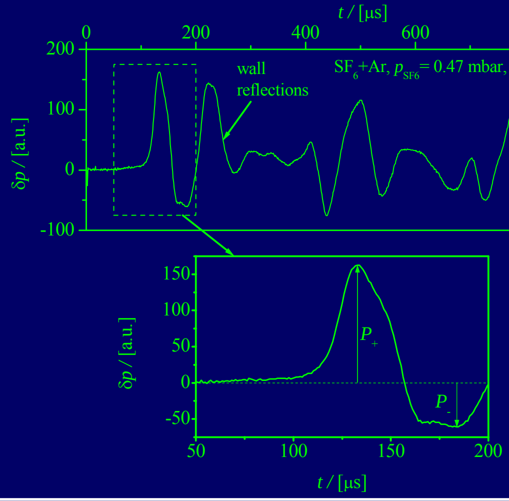


Photoacoustic Spectroscopy and Sample Excitation

Air Monitoring by Photoacoustic Spectroscopy

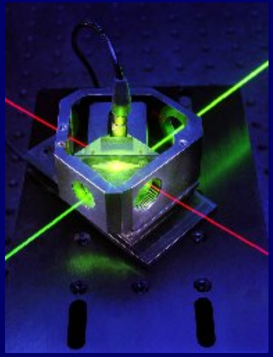


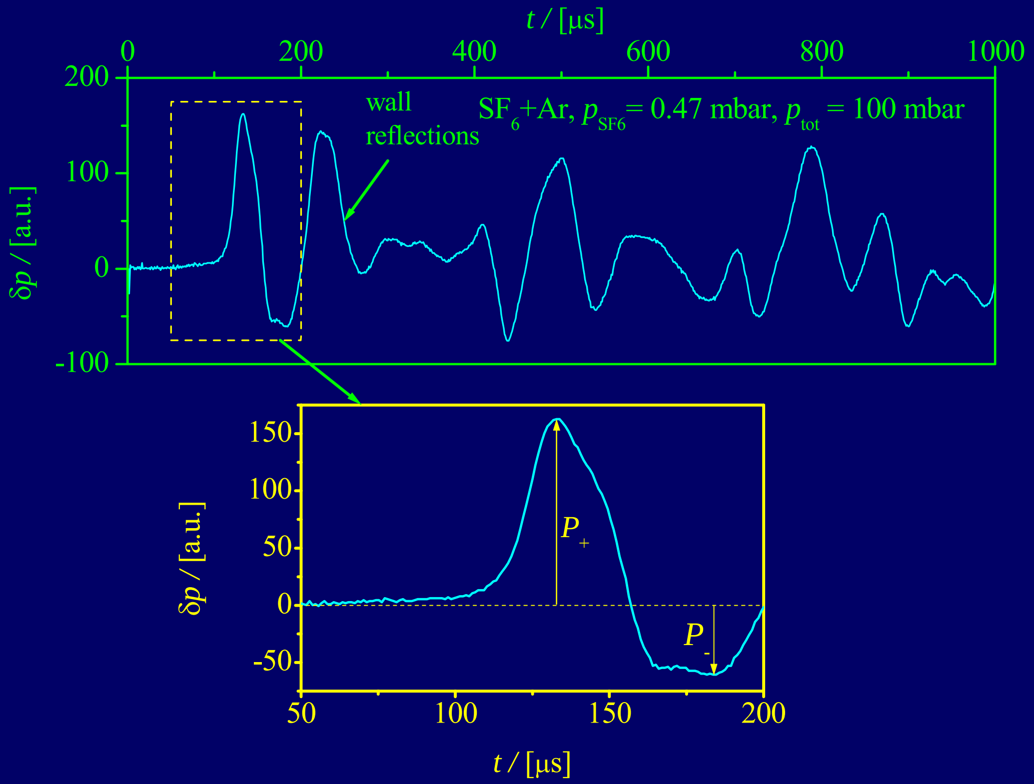




Experimental Set Up for Pulsed PAS

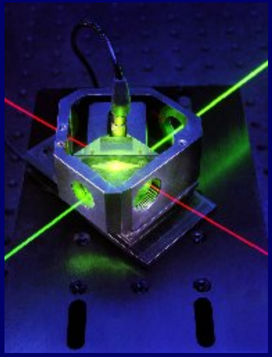
Air Monitoring by Photoacoustic Spectroscopy

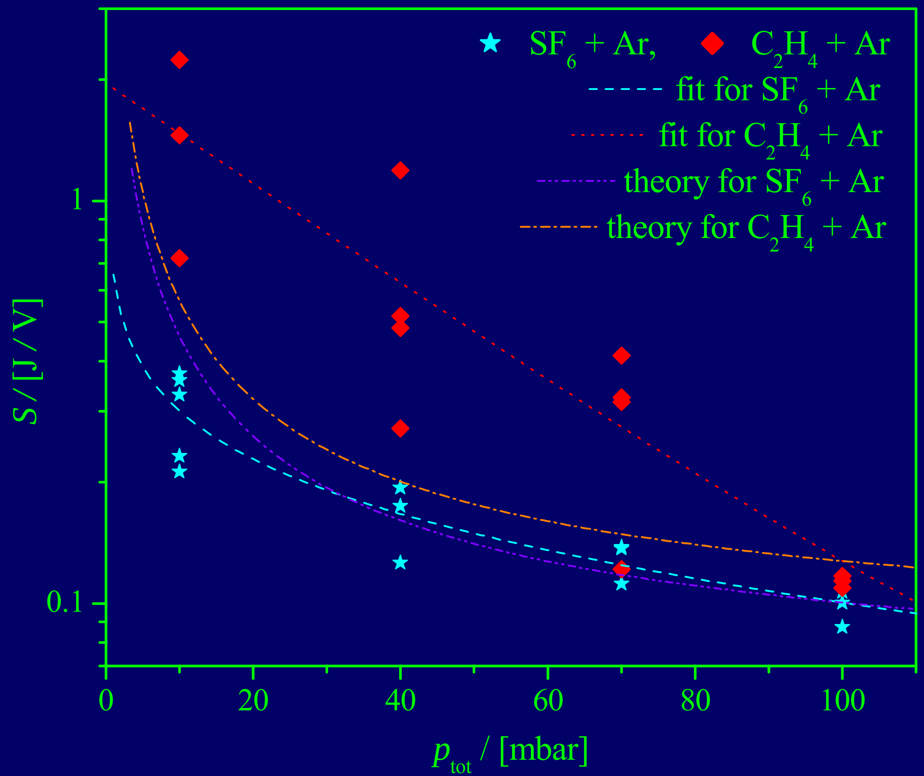




Photoacoustic signal

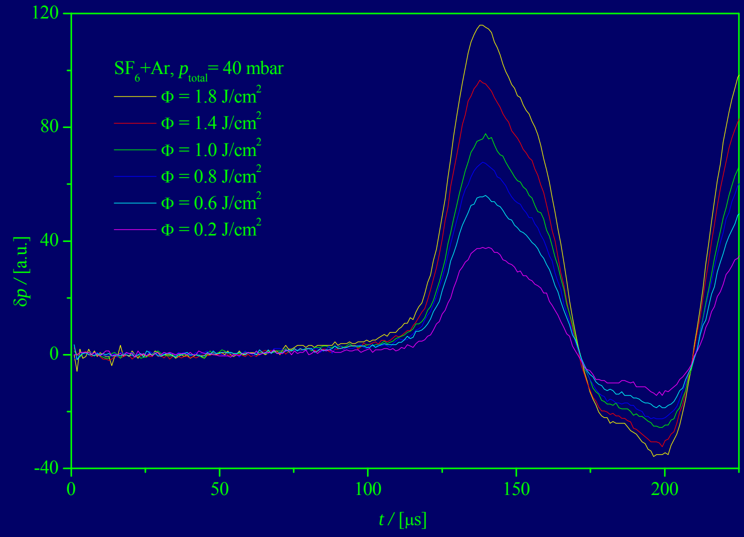
Air Monitoring by Photoacoustic Spectroscopy

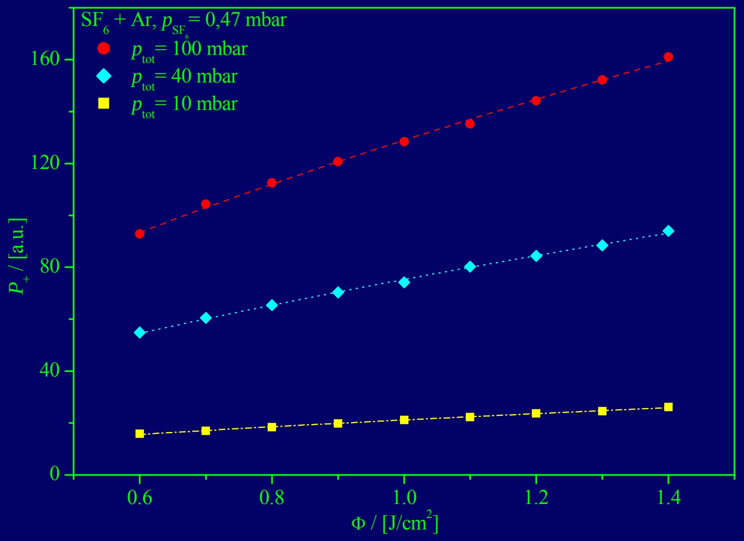




Semi theoretical "one point" calibration

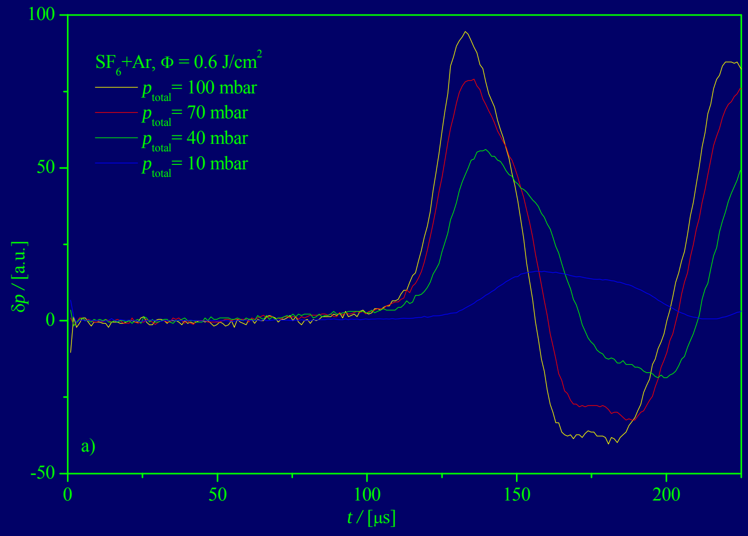
Air Monitoring by Photoacoustic Spectroscopy

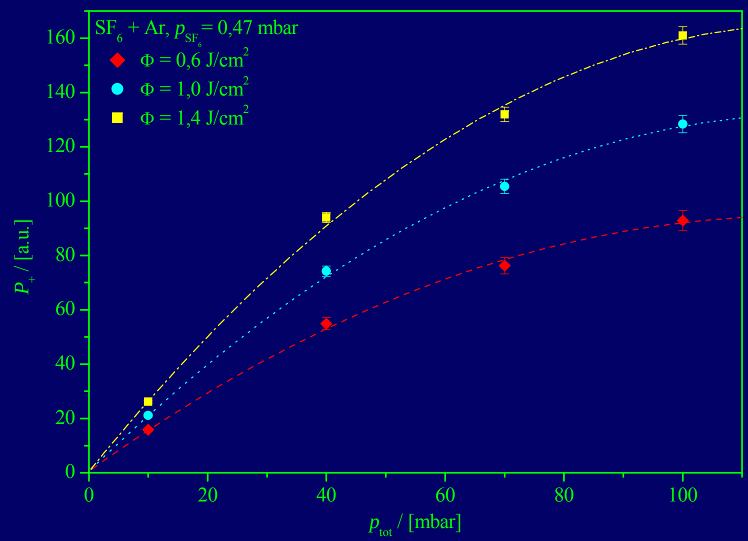


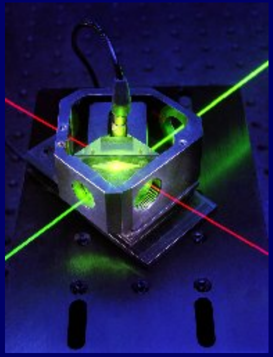


Energy and pressure dependent analysis

Air Monitoring by Photoacoustic Spectroscopy

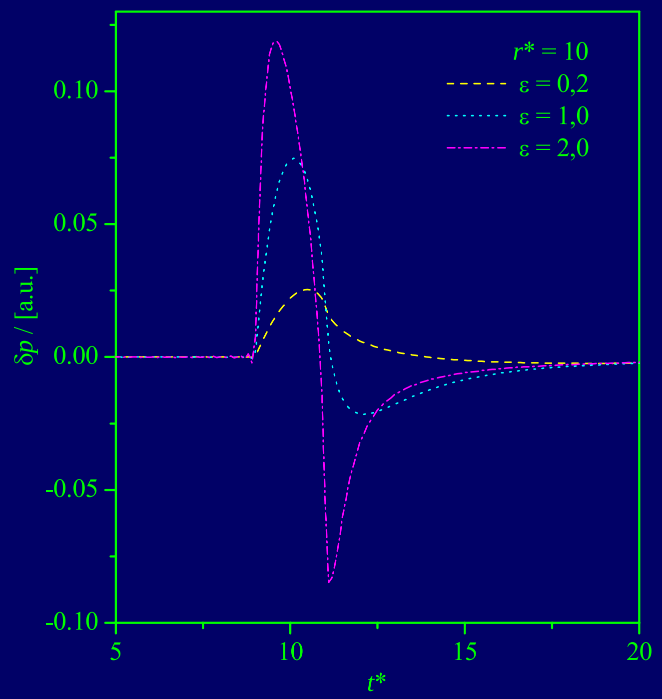


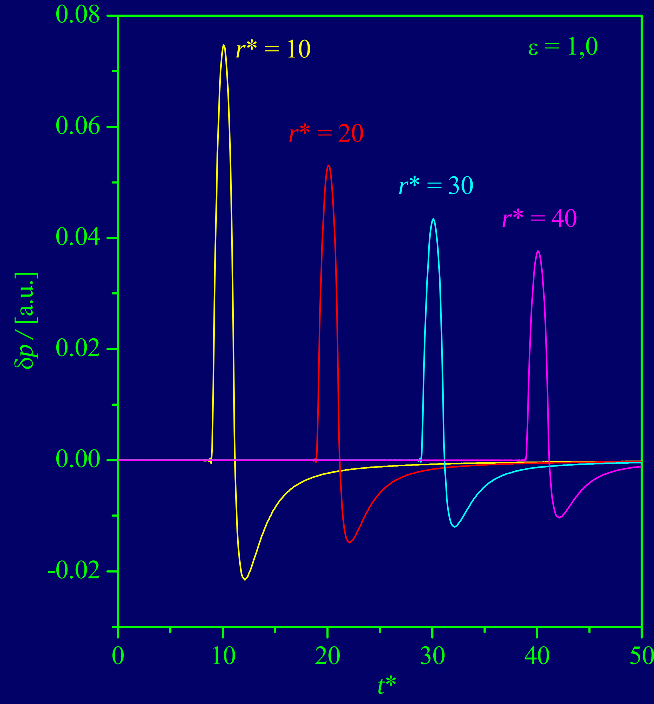


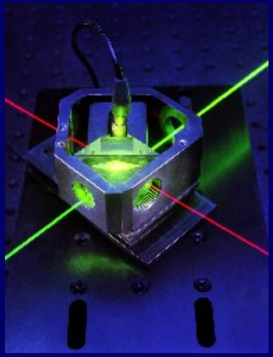


Energy and pressure dependent analysis

Air Monitoring by Photoacoustic Spectroscopy

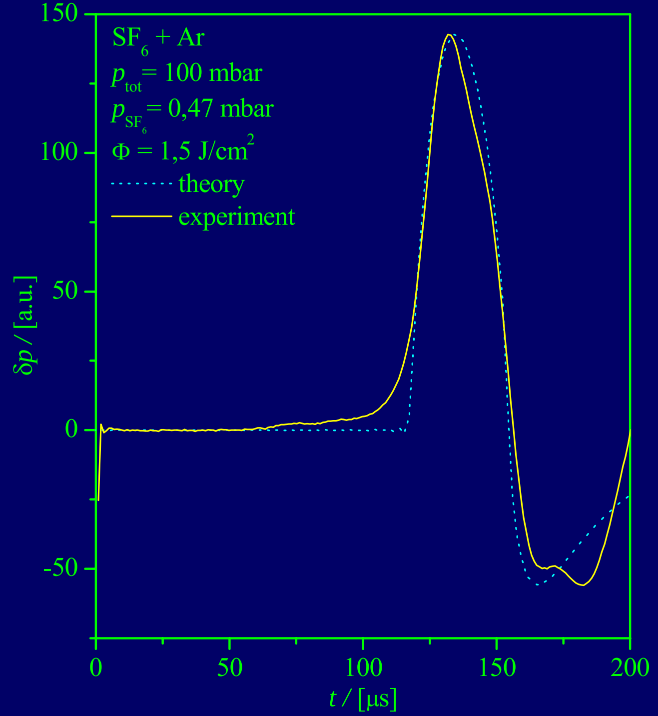


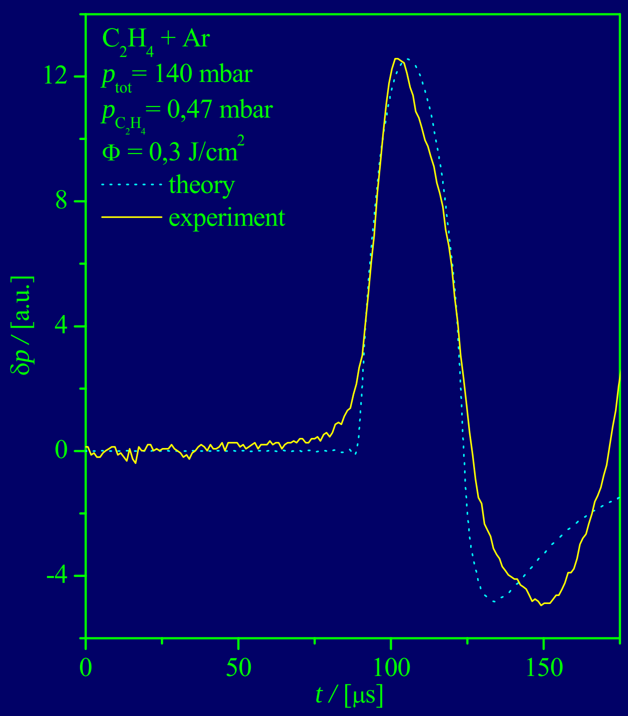


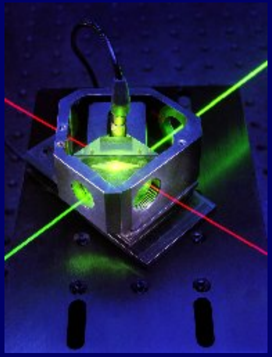


Relaxation parameters calculation

Air Monitoring by Photoacoustic Spectroscopy

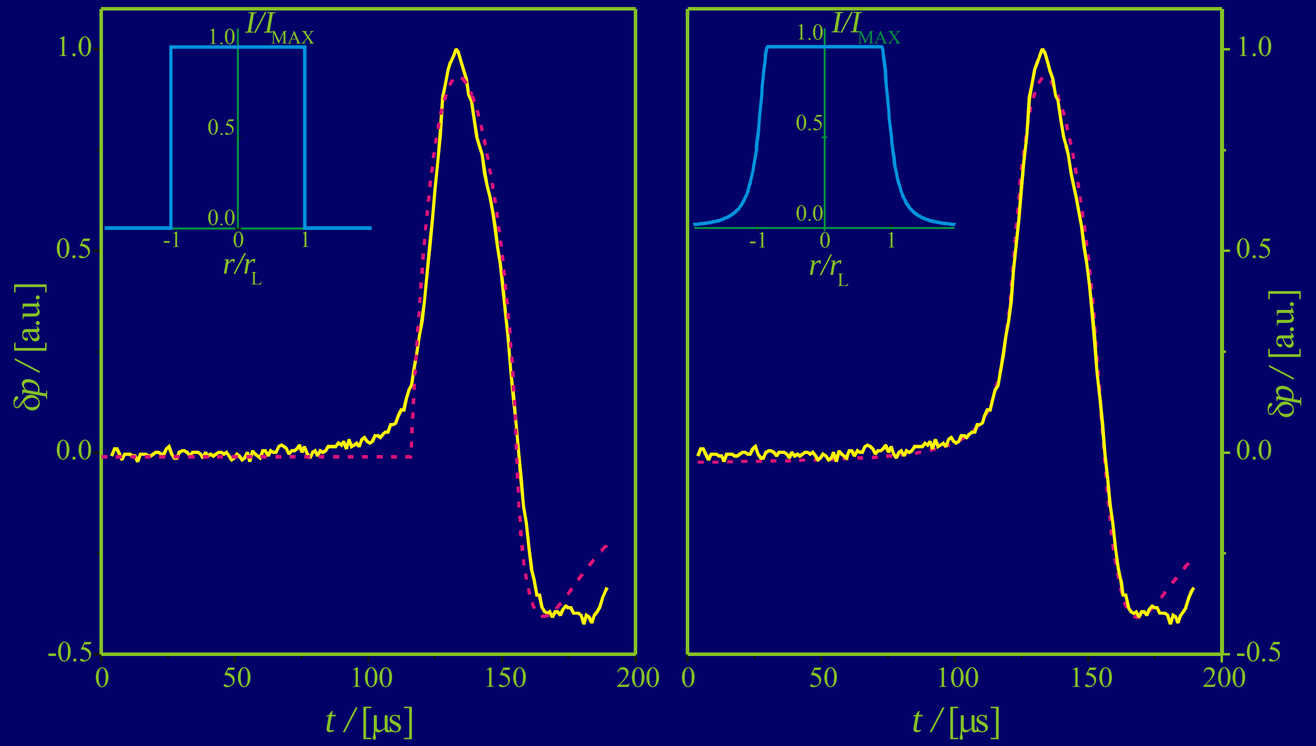


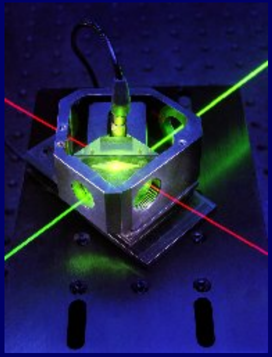




Theoretical and experimental signals

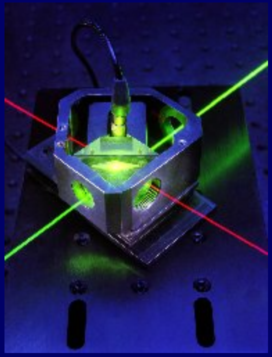
Air Monitoring by Photoacoustic Spectroscopy

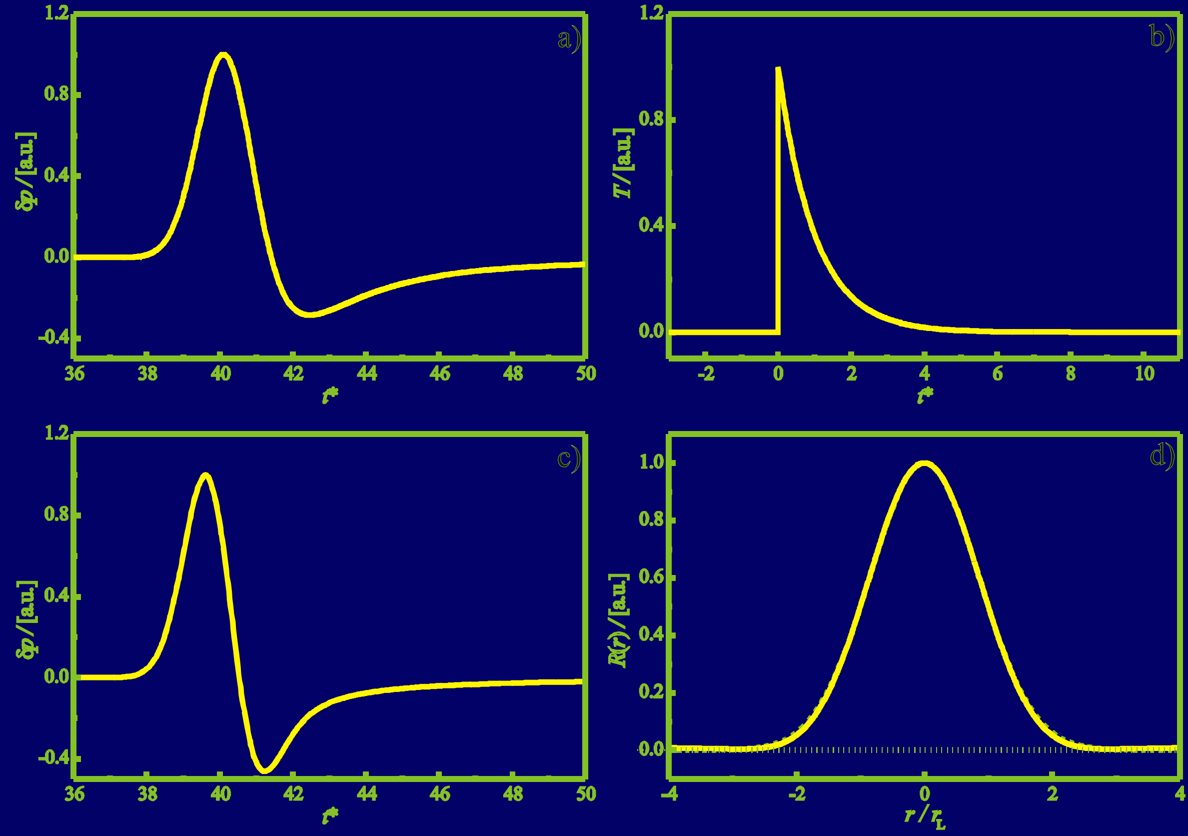




Theoretical and experimental signals

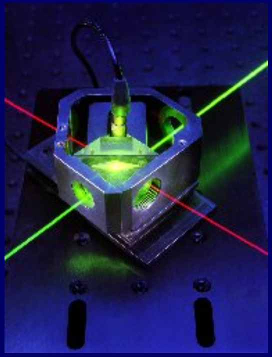
Air Monitoring by Photoacoustic Spectroscopy

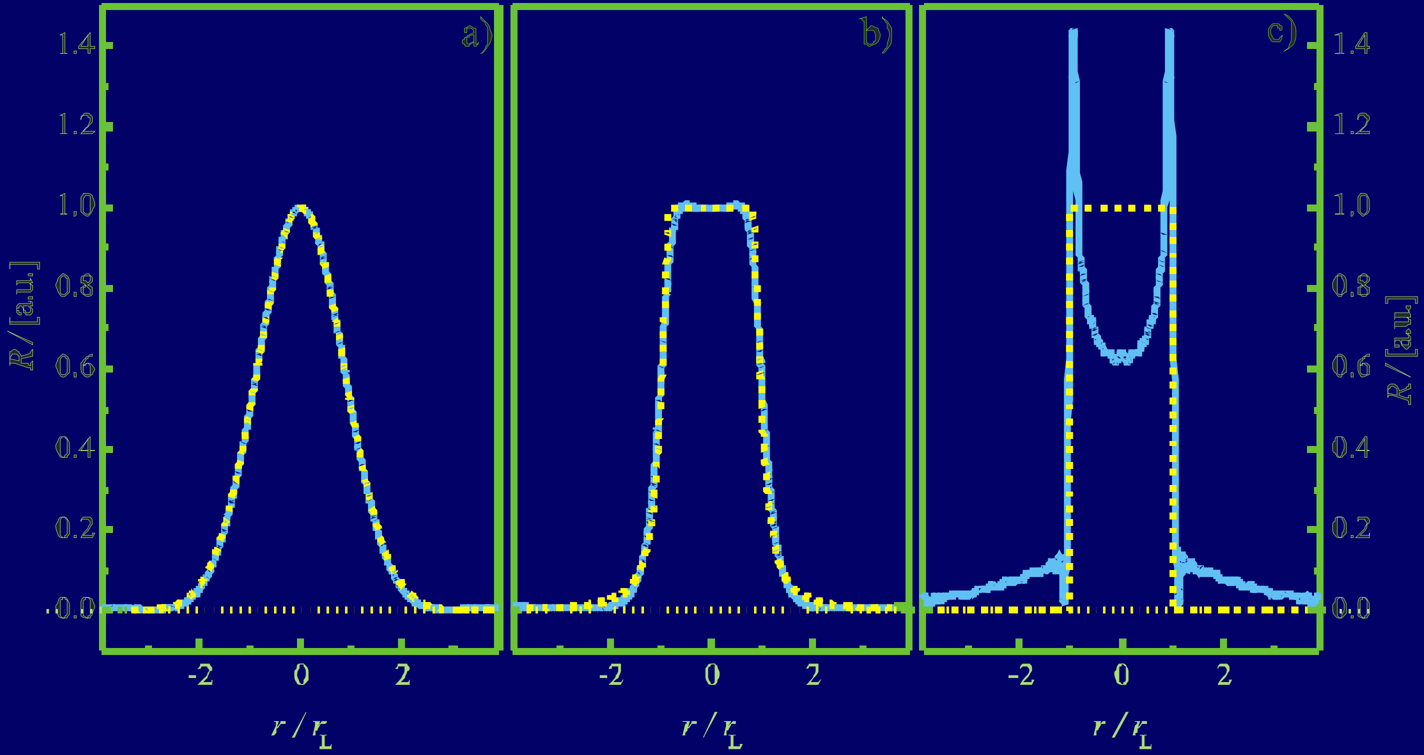




Photoacoustic Tomography Adapted For Gases

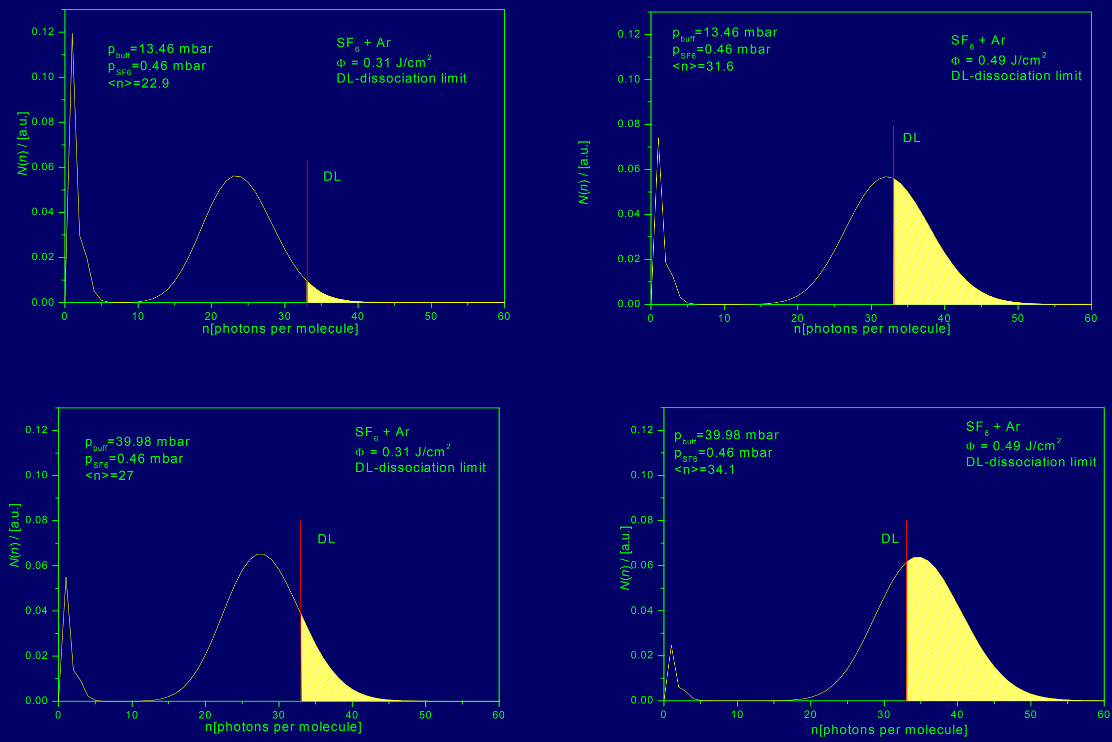
Air Monitoring by Photoacoustic Spectroscopy

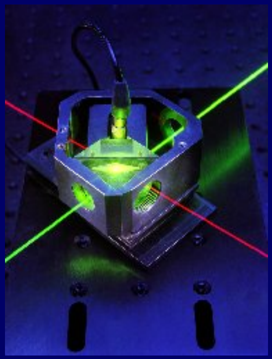




Photoacoustic Tomography Adapted For Gases

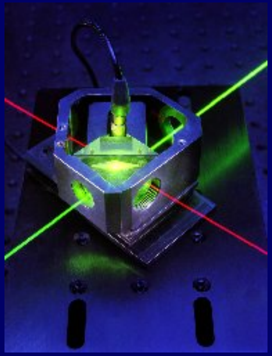
Air Monitoring by Photoacoustic Spectroscopy

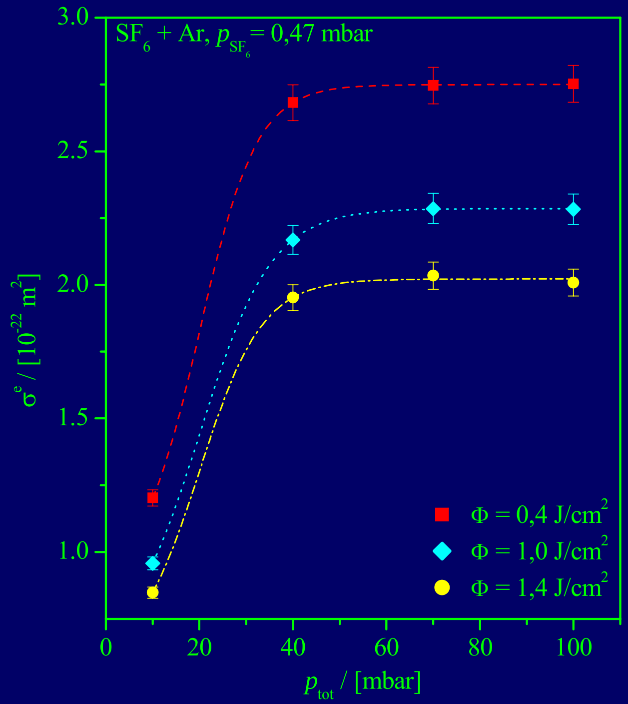


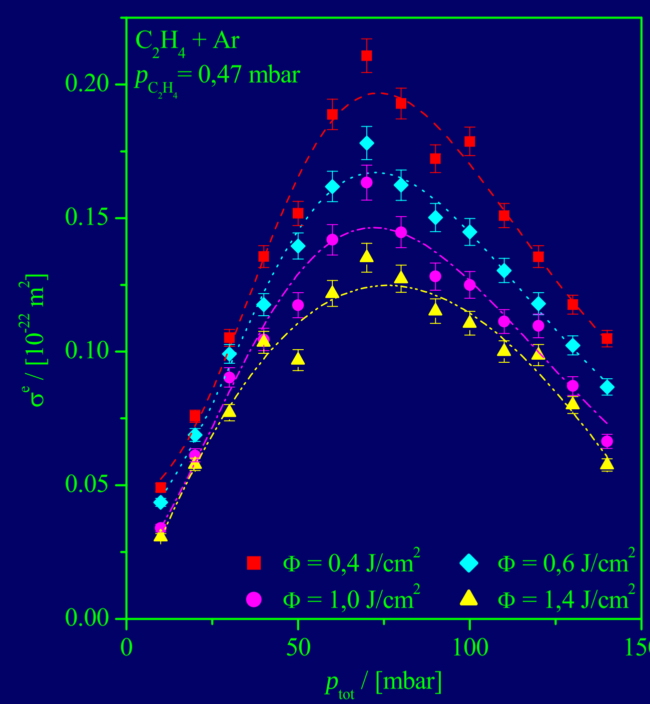


Collisional influence through rotational relaxation

Air Monitoring by Photoacoustic Spectroscopy

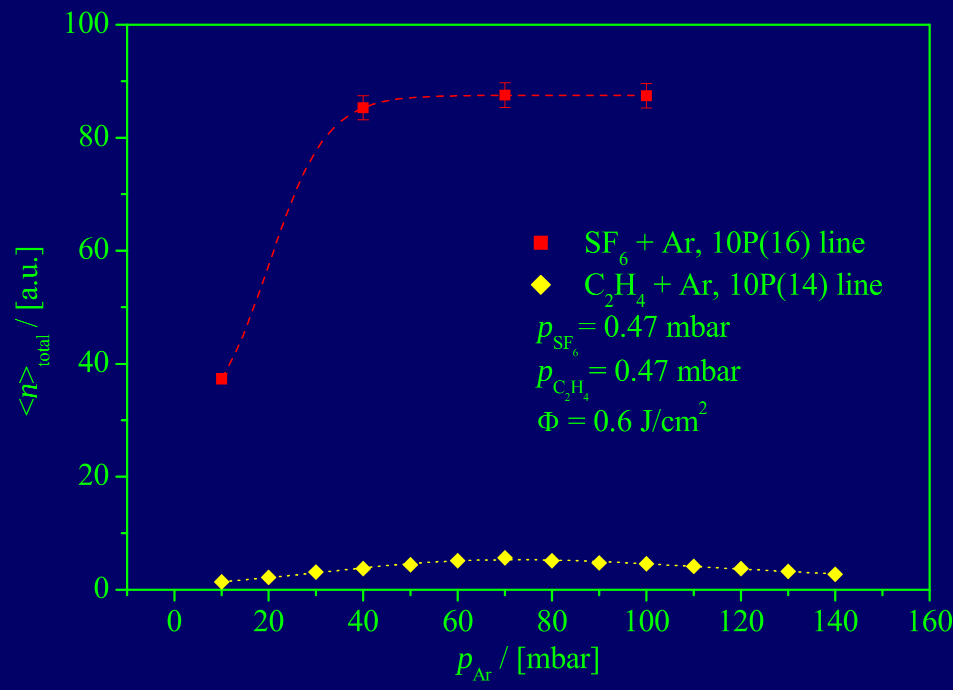


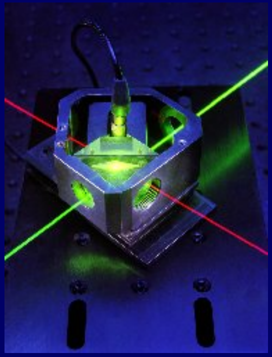




Absorption characteristics of irradiated molecules

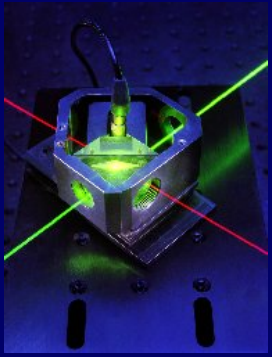
Air Monitoring by Photoacoustic Spectroscopy





Comparison between two absorbers

Air Monitoring by Photoacoustic Spectroscopy

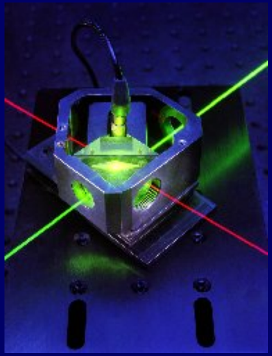


- Recent investigation shows that, currently, we are far away from a stagnation of the trace gases concentration levels in the atmosphere. This is the reason why study of them and their behavior in different gas mixtures is very important to understand their environmental behavior.
- Beside this, every problem which could arise from some phenomena within the frame of environmental studies could be explained also in the terms of physics.
- To understand the PAS one must have basic knowledge of atomic and molecular physics, quantum optics, oscillation and sound, etc.
- But there are some phenomena that are well known and global, but could be explained much easier.

Air Monitoring by Photoacoustic Spectroscopy

Global warming can be defined as an observed increase in the average temperature of the Earth's atmosphere and oceans in recent decades.

An increase in global temperatures can in turn cause other changes, including a rising sea level and changes in the amount and pattern of precipitation. These changes may increase the frequency and intensity of extreme weather events, such as floods, droughts, heat waves, hurricanes, and tornados.



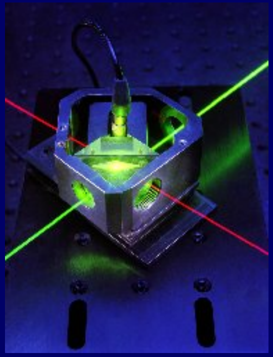
Other consequences include higher or lower agricultural yields, glacial retreat, reduced summer stream flows, species extinctions and increases in the ranges of disease vectors.

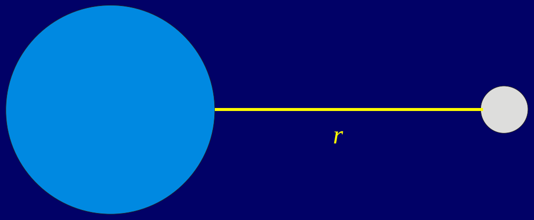
Air Monitoring by Photoacoustic Spectroscopy

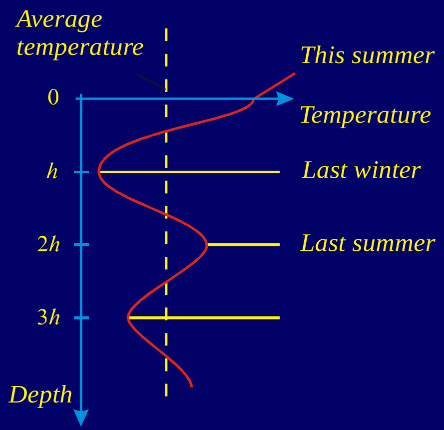
Beside these, global warming and other environmental problems could have a non negligible influence (direct or indirect) on some other natural phenomena such as:

a) Motion in a gravitational field: Earth – Moon system

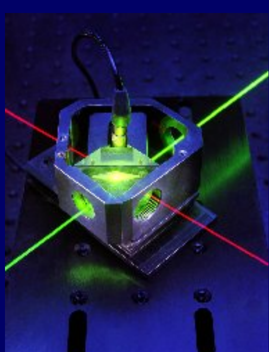
b) Heat conduction and species extinction





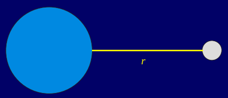


Air Monitoring by Photoacoustic Spectroscopy



- Melting of the ice caps on our planet causes the rising of the oceans level. Also gravitational influence of the Moon periodically raise and lower the level of water in the oceans, and this phenomenon is manifested at the shores in the form of tides and ebbs.
- Tides cause a motion of the water masses at the Earth surface and this is accompanied by friction and a loss of energy in performing work against the frictional forces.
- This results in a tide producing force, which leads to a decrease in the velocity of the Earth’s rotation. The tide-producing force on the Earth increases its period of revolution about its axis by 4.4×10^{-8} s per revolution. Such decrease is confirmed by the astronomical observations.

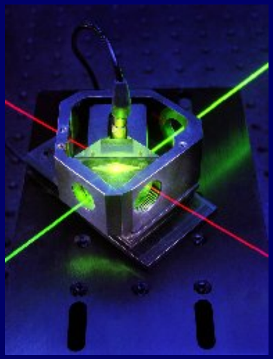
Air Monitoring by Photoacoustic Spectroscopy



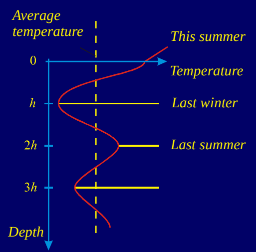
- It is well known fact that the Earth revolves about its axes (having an angular momentum L_E) in the same direction in which the Moon rotates around the Earth. The Earth and Moon are rotating around their common centre of the mass (having an angular momentum L_{EM}). The total angular momentum of the Earth – Moon system must be conserved (L_t).

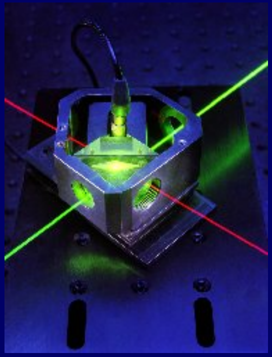
$$L_t = L_E + L_{EM} = const.$$

- Hence a decrease in the angular momentum of the Earth L_E must be accompanied by an increase in the angular momentum L_{EM} of the Earth – Moon system moving around their common centre of the mass (conservation law).
- An increase in the L_{EM} due to tide – producing force leads to an increase in the distance between the Earth and the Moon. The rate of increase is about 0.04 cm/day.
- What rate of increase will be after the ice cap melting?



Air Monitoring by Photoacoustic Spectroscopy



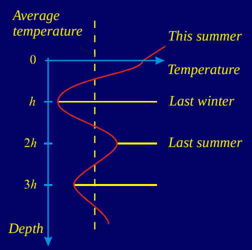


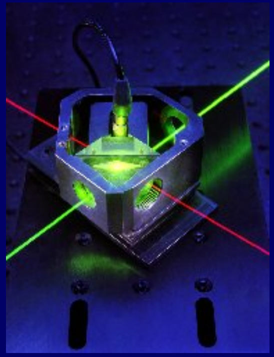
It is also a well known fact that some species built their homes and shelters on certain depth underground. This is their natural behavior which could be explained also in the terms of general physics (thermodynamics).

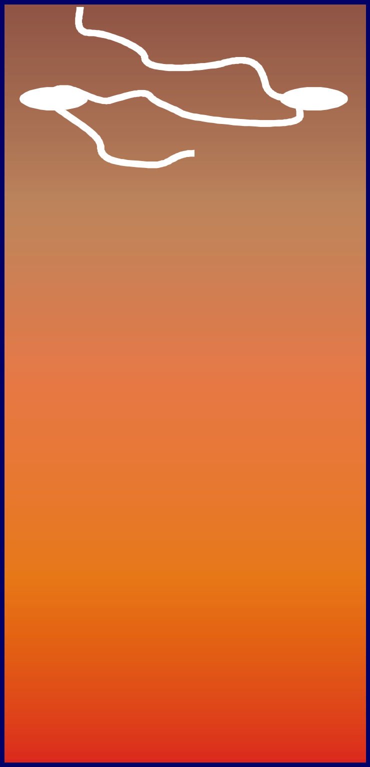
Those shelters protect them not only from their enemies, but from the extreme weather conditions, especially high temperatures during the summer and low temperatures during the winter seasons.

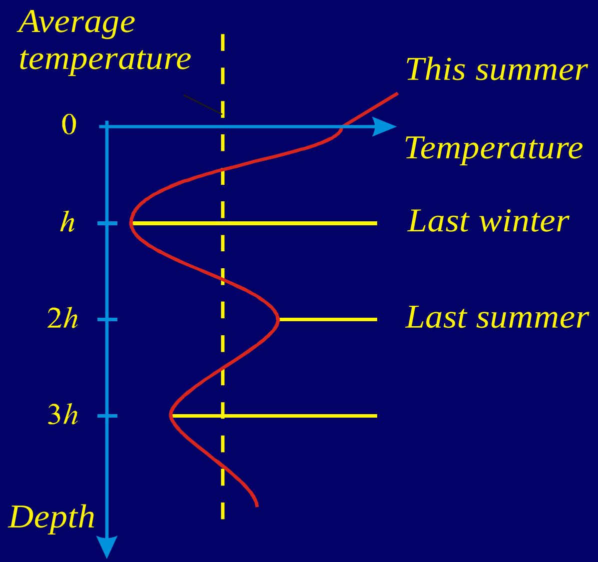
Special attention has to be paid on soil composition at the surface of the Earth and on the depths from 0 to 20 m from the surface. Heat conduction efficiency is a thermodynamic parameter which could give you some important information and answers about this phenomenon.

Air Monitoring by Photoacoustic Spectroscopy









$$\lambda = \frac{hQ}{S\Delta Tt} \cdot \frac{m}{m} \approx \frac{hmc}{St} = \frac{h\rho Vc}{St} = \frac{h\rho hSc}{St} = \frac{h^2\rho c}{t},$$

$$h \approx \sqrt{\frac{\lambda}{\rho c} t} = \sqrt{\frac{\lambda}{\rho c}\frac{T}{2}} = \sqrt{3}\ \text{m}.$$

Air Monitoring by Photoacoustic Spectroscopy

- Literature

- [1] Sigrist M W, *Air Monitoring by Spectroscopy Techniques*, ed M W Sigrist (New York: John Wiley & Sons, 1994) p 127
- [2] Sigrist M W, *Rev. Sci. Instrum.* **74** (2003) 486, http://dx.doi.org/10.1063/1.1512697
- [3] Jalinik H, Bicanic D, Franko M and Bozóki Z, *Appl. spectrosc.* **49** (1995) 994, http://dx.doi.org/10.1366/0003702953964877
- [4] M. D. Rabasovic, D. D. Markushev and J. Jovanovic-Kurepa, *Measurement Science & Technology*, **17**, **No7** (2006) 1826-1837, http://www.iop.org/EJ/abstract/0957-0233/17/7/022
- [5] M. D. Rabasovic, J.D. Nikolic and D. D. Markushev, *Measurement Science & Technology*, **17, No 11,** (2006) 2938-2944, http://www.iop.org/EJ/abstract/0957-0233/17/11/011
- [6] Mira Terzic, Dragan D. Markushev, Mihajlo Rabasovic, *Acta Chimica Slovenica* **53**, (2006), 65-71, http://acta.chem-soc.si/53/53-1-65.pdf
- [7] Terzić M, Markušev D D and Jovanović-Kurepa J, *J. Phys. B* **32** (1999) 1193, http://dx.doi.org/10.1088/0953-4075/32/5/012
- [8] Markushev D D, Jovanović-Kurepa J and Terzić M, *J. Quant. Spectrosc. Radiat. Transfer* **76** (2003) 85, http://dx.doi.org/10.1016/S0022-4073(02)00047-X
- [9] J. Gajević, M. Stević, J. Nikolić, M. Rabasović, D. Markushev, *Facta Universitatis, Series: Physics, Chemistry and Technology*, **Vol. 4, No 1,** (2006), pp. 57 – 69, ISSN 0354-4656, http://facta.junis.ni.ac.yu/facta/phat/pcat2006/pcat2006-06.pdf