INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O. B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392 - I

SMR/115 - 41

WINTER COLLEGE ON LASERS, ATOMIC AND MOLECULAR PHYSICS

(21 January - 22 March 1985)

ATMOSPHERIC MOLECULES

C. MULLER
Institut d'Aéronomie Spatiale de Belgique
Avenue Circulaire, 3
1180 Brussels
Belgium

INTERNATIONAL CENTER FOR THEORETICAL PHYSICS

MARCH 1985

ATMOSPHERIC MOLECULES

C. MULLER
Institut d'Aéronomie Spatiale de Belgique
Avenue Circulaire, 3
B-1180 BRUSSELS, Belgium

Lecture 1

The Earth's atmosphere

- Composition and formation
- Physical properties
- The troposphere
- The stratosphere
- The mesosphere
- The thermosphere

Lecture 2

Penetration of solar radiation

- An overview of the solar spectrum
- U.V. radiation and environmental effects
- Visible radiation
- Infrared spectrum

Lecture 3

Infrared spectroscopy and the atmosphere

- Introduction
- A reminder of absorption laws
- Line shape
- Line parameters
- Individual molecules in the atmosphere.

Lecture 4

Observation techniques

- Observation geometries
- Inversion of data
- Instrumental requirements
- Individual instruments and observation results.

FOREWORD

These short notes on the course "atmospheric molecules" do not intend to replace any textbook on atmospheric physics, spectroscopy or environment science. Their only purpose is to give a structuring skeleton to these lectures. It is difficult to cover, even in a one year course, all the aspects of radiative aeronomy; however, I have attempted to show how this subject can be relevant to the molecular scientist and these lectures will be successful if they inspire a development of worldwide observations of our atmosphere which is one of our few undivisible ressources.

LECTURE 1

THE EARTH'S ATMOSPHERE

Composition and formation

The atmospheric gas is composed of 78.1% of nitrogen (N_2), 20.9% of oxygen (O_2) and 1% of argon (A). Argon is entirely inert, N_2 in a first approximation could be considered as inert too while already at ground level O_2 is involved in chemical reactions.

The other components of clean air expressed in volume mixing ratio are : neon (18 ppm), helium (5.2 ppm), krypton (1.1 ppm), xenon (0.09 ppm); CO_2 (340 ppm), hydrogen (H_2) (0.5 ppm), CH_4 (1.6 ppm), N_2O (0.3 ppm). Water vapor also exists in extremely variable concentrations ranging from saturation down to the stratospheric value of 3 ppm. Ozone (O_3) is a tropospheric constituent too but its high reactivity leads to ground level values which proves to be highly variable. This list is far from exhaustive and several thousands of gases have already been considered in all kinds of atmospheric and environment problems; this course will limit itself to gases interacting significantly with radiation and which present a global environmental impact.

Geological studies show that atmospheric composition has evolved since the beginning of the earth; it is estimated that oxygen did not play any role up to 1.8 billion years ago while it has been present for the last 1.4 billion years, the main present source of atmospheric oxygen being organic photosynthesis, this oxygen being, in turn, the support of all aerobic life including ours.

The primitive atmosphere was composed of mainly reducing gases : H_2, N_2, CO_2, A, CH_4, H_2O and trace of other gases, volcanic activity contributed rapidly to the release of water vapor from hydrated mineral until the oceans formed. Oxygen was then present as a trace gas related to photochemical reactions of H_2O. Anoxygenic microorganisms probably evolved slowly in the oceans and underground, shielded from hard unfiltered U.V. radiation. Two steps are speculated first when 1% O_2 was reached, the microorganisms passed the "Pasteur point" where they could benefit from the much higher energetic yield of respiration compared to their previous fermentation mode. The multiplication of microorganisms adapted to oxygen led to an increase of photosynthesis which resulted in the second step : at 1/10 of present level, a significant ozone filter began to build up in the upper atmosphere and life could colonize the continents. These two steps identify with the beginnings of the cambrian and of the silurian (~ 500 million years and 450 million years ago).

Physical properties

In a first approximation, the atmosphere can be seen as a perfect gas submitted to the hydrostatic equation :

$$\rho = -\frac{1}{g}\frac{dp}{dz}$$

in which ρ is the density, p the atmospheric pressure and g the acceleration of gravity at altitude z, this relation combined with

$$p = n\,k\,T$$

where n is the molecular concentration and k the Boltzmann's constant, leads to

$$\frac{dp}{p} = -\frac{dz}{kT/mg}$$

which integrates in $p = p_o\, e^{-z/H}$,
H being the scale height defined as $H = \frac{kT}{mg}$.

This simple formalism leads to a decrease in pressure with altitude, meaning an adiabatic expansion of a perfect gas and thus a corresponding cooling. This view was contradicted when eighty years ago the French meteorologist Teisserenc de Bort initiated a serie of balloon flights of recording thermometers up to the altitude of 14 km. He discovered that above 10-12 km, the temperature stopped decreasing and in some cases seemed to increase. This so-called inversion layer cannot maintain convection and Teisserenc de Bort named it stratosphere : zone of layering, and the lower region received the name of troposphere : zone of mixing. Fifty years later, the analysis of high altitude balloon and rocket soundings led to the temperature profile of fig. 1.1 and the presently accepted nomenclature of atmospheric regions.

The main nomenclature is based on the temperature gradients : troposphere, stratosphere, mesosphere and thermosphere; an other division is based on diffusion properties : the homosphere, corresponding in the mixing of the major gases, while, above 100 km, in the heterosphere, the gases diffuse according to gravity and eddy diffusion is no longer the major transport process.

__The troposphere__

The tropospheric temperature varies between about 300 K at ground level, with a latitudinal and seasonal variation of up to 50 K, to a lower temperature of about 200 K at the tropopause, its summit which range from as low as 8 km in the winter pole to a high as 16 at the equator. This gradient leads to strong convective motions which coupled with variable quantities of water vapor leads to very effective dynamical process. The water vapor, ascending to cooler regions reaches its condensation point and tend to form droplets around condensation nuclei which finally lead to precipitations. Tropospheric photochemistry must thus be considered in the presence of washout processes and very fast mixing. A large number of gases are continuously introduced in the

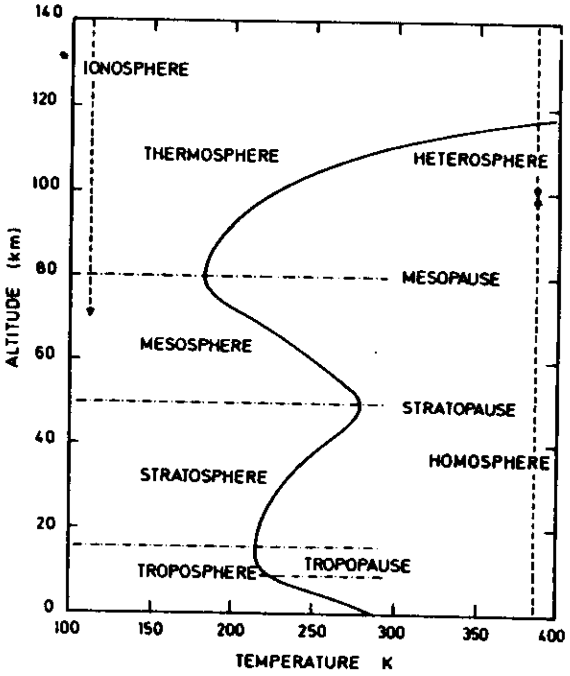

__Fig. 1.1__ Conventional division of the atmosphere into zones corresponding to the temperature profile; two lines are indicated at the tropopause level to show the variation between the tropical summer tropopause of about 18 km and the polar winter tropopause sometime as low as 8 km.

troposphere by anthropogenic activities or natural sources : examples of such production are :

- N_2O : originating in the denitrification of acid soils by anaerobic bacteries
- CH_4 : produced by the decay of organic biomass through fermentation processes
- CO_2 : product of organic respiration and fossil fuel burning, naturally controled by the oceans and consumption by the biomass
- NO, NO_2, HNO_3: could be produced by lightning and industrial sources, sensitive to washout, create the catalytic chain of smog in sunlit urban atmosphere, otherwise, their washout contributes to the acid rain problem of the Northern temperate lattitudes
- CO : produced by numerous microorganisms and in the cities by exhaust gases
- SO, SO_2, SO_3, H_2SO_4 : industrial products, fossil fuel burning residues or direct volcanic products, are thought to be the main source of acid rain
- Freons ($CFCl_3$, CF_2Cl_2) : pure products of human activities, rare example of gases with no known losses in the troposphere, are directly transported to the stratosphere
- O_3 : product of local smog-like reactions or transported from the stratosphere; ozone as a strong oxidant is one of the main agents of smog health hazards and damages to property
- HF, HCL : product of industrial processes but their extreme reactivity and water solubility prevent them from being more than a local problems; in some limited cases, they are directly injected in the stratosphere by volcanic eruptions.

Several hundred of other gases are injected in the troposphere and could have local environmental impacts, a few, as the ones quoted above have also global consequences; optical techniques permit a verifiable monitoring of all these constituents and demand the knowledge of their spectral properties.

The stratosphere

The very low temperature at the bottom of the stratosphere acts as a water trap and limits the stratospheric water vapor concentration to about 3-5 ppm, the conditions to produce clouds in the stratosphere are thus never reached except in some rare arctic occurences. The main feature of the stratosphere is the presence of an ozone layer which acts as an effective filter for ultraviolet radiation of wavelengths shorter than 300 nm. It was discovered in 1880 by astronomers studying the ultraviolet limit of the solar spectrum from mountain stations. The vertical distribution of O_3 could, however, only be determined between 1920 and 1930 when instrumental developments in the U.V. allowed Fabry and Buisson in Marseille, Dobson in Oxford and Götz in Arosa to perform quantitative observations of atmospheric ozone. They rapidly deduced that the width of the layer reduced to ground pressure was only about 3 mm. The distribution with altitude was determined by Götz by studying zenithal diffuse light as a function of the zenith angle of the Sun, he could see that the maximum of absorption of scattered U.V. radiation was above the tropopause, in the 25 km range of altitude. This ozone maximum and the corresponding U.V. radiation absorption is the main factor in the stratospheric temperature increase.

The first theoretical explanation of the generation of the ozone layer was introduced by Chapman in 1930 leading to the intervention of the atomic oxygen atom O :

$$O_2 + h\nu \rightarrow O + O \qquad \lambda < 240 \text{ nm}$$

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

$$O_3 + h\nu \rightarrow O_2 + O \qquad \lambda < 310 \text{ nm}$$

This simple mechanism shows the potential instability of the stratospheric ozone layer : ozone is simultaneously produced and destroyed and is thus sensitive to all kind of perturbations, and more : the reaction rates are dependant on temperature which itself is driven by the ozone concentration.

The Chapman mechanism represents correctly the ozone layer but fails in the upper stratosphere by predicting ozone densities which are higher than those observed. The mechanism was altered only in 1950 when the successive discoveries of the OH emission in the airglow and of the importance of NO in the mechanism of ionosphere formation led Bates and Nicolet to introduce a more realistic chemistry.

The chemistry of ozone has been discovered since 1970 to be sensitive to anthropogenic perturbations through a serie of catalytic reactions which destroy both atomic oxygen and ozone ; the two best investigated cycles are :

$$\begin{array}{lcl} NO_2 + O & \rightarrow & NO + O_2 \\ NO + O_3 & \rightarrow & NO_2 + O_2 \\ \hline O + O_3 & \rightarrow & 2O_2 \end{array}$$

and

$$\begin{array}{lcl} ClO + O & \rightarrow & Cl + O_2 \\ Cl + O_3 & \rightarrow & ClO + O_2 \\ \hline O + O_3 & \rightarrow & 2O_2 \end{array}$$

Nitrogen oxides and chlorine could be introduced by human perturbations as high flying stratospheric aircrafts, transport of increased tropospheric N_2O or in the case of chlorine, photodissociation of "freons".

An even more efficient chain could be built with bromine, happily industrial use of bromine based fluorocarbons is still very limited but is growing due to their use in fire extinguishers.

The concern for damage to the earth's ozone layer has been a permanent drive for stratospheric research in the last 15 years.

The mesosphere

Above the ozone maximum, temperature begins to stop increasing and even decreases at altitudes higher than about 55 km. The name mesosphere indicates an intermediate layer between the stratosphere, dominated by the ozone problem and the upper layers which were studied because of their ionic layers; moreover, until the very last years, the mesosphere was largely unmapped because it cannot be reached by balloons and the rocket measurements tend to have their better efficiency at higher altitudes. Now data from specialized satellites and orbital stations like Spacelab tend to improve rapidly the current view and prove that this zone as photochemically complex and indispensable to the understanding of the entire atmospheric balance.

Satellite observations, especially by the limb sounding technique, necessitate an understanding of low pressure spectra of all atmospheric molecules. Up to now, the main application effect of a phenomenon happening in the mesosphere was the photoionization of nitric oxyde by solar extreme U.V. radiation :

$$NO + h\nu \ (\text{Lyman } \alpha) \rightarrow NO^+ + e^-$$

This mechanism, recognized by Nicolet in 1945, leads to the buildup of the ionospheric D layer which is important for the understanding of radiopropagation and its perturbations.

The thermosphere

Above 100 km, the collisions between molecules become negligible and the temperature increases up to values which are mainly dependant on solar activity, this region benefitted a lot from early space flights because the decays of the orbits of the first satellites proved to be much higher than expected, leading to a renewed interest in the solar earth-relationship.

LECTURE 2

PENETRATION OF SOLAR RADIATION

An overview of the solar spectrum

The sun is composed of hydrogen and helium with a few metallic traces. In its center, a chain of thermonuclear reactions converts atomic hydrogen into helium and the corresponding energy is transported by radiative and convective processes to its visible outer limit which is called the photosphere. The depth of this layer is about 1000 km and its effective temperature is around 6000 K allowing the formation of the CO molecule. Granulation on the sun reveals intense convective processes which from time to time lead to the formation of sunspots which are regions of several time the earth's surface where the temperature is lower ($\approx$3000 K), associated with high temperature regions called faculae. Their periodicity of observation is about 11 years and they are associated with energy bursts.

The first possible representation of the solar spectrum is a blackbody at 5975 K, its radiated energy is represented by the Stefan-Boltzmann law :

$$M_E = \sigma T^4$$

which has to be reduced by a dilution factor to get the energy received at the top of the atmosphere :

$$S_e = \beta_g M_E$$

where the delution factor $\beta_g = \frac{R_s^2}{4r_s^2}$, R_s being the solar radius and r_s the sun-earth distance. Its maximum is attained in January and its minimum in July, giving an energy input variation of 6.6%. The possible variation with time of the solar "constant" is presently a much debated subject and is addressed by several space experiments.

The maximum intensity of the solar spectrum represented on figure 2.1, is as expected in the visible, near 500 nm, at the transition between the blue and the green colors. Departure from the blackbody becomes significant below 300 nm where the solar spectrum is better fitted by lower temperatures (4500-5000 K). For our purpose, the most important deviation is the hydrogen Lyman α emission line at 121.6 nm which, due to its high energetic yield has a major influence on the photochemistry of the upper mesosphere.

U.V. radiation and environmental effects

For medical and environmental applications, three spectral division have been established : U.V.C for $\lambda < 280$ nm, U.V.B for $\lambda > 280$ nm and < 320 nm and U.V.A above 320 nm. The erythemal action spectrum (fig. 2.2) has been the main drive for this choice. The erythemal action effect has a minimum at 280 nm, a strong peak near 300 nm and becomes negligible above 320 nm. The erythema is important in itself as it leads to human skin cancer, it is also parallel to the action effect of radiation on mammalian D.N.A. cells, it is now thought that damages to D.N.A. represent initiating events in carcinogenesis.

Biological effects on plants are less well known, while an increase of blue and near U.V. radiation is favorable to growth, U.V.B. slows the rate of photosynthesis and finally leads to a thickening of the leaves and the death of the plant.

The relation rates between increased U.V. radiation and a particular pathology are extremely difficult to determine, due to the number of factors involved. As will be shown soon, O_3 is the main shield for U.V.B., it is generally stated that for a 1% ozone decrease, skin cancer increases by 2%.

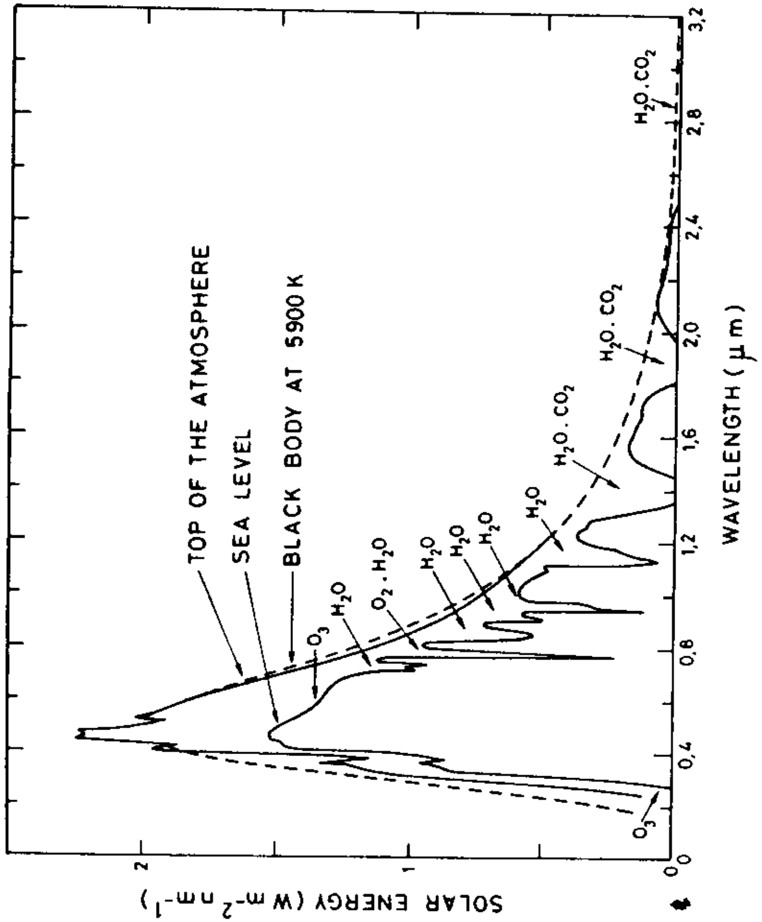

Fig. 2.1. Solar spectrum in its main energetic region compared with a blackbody spectrum and spectrum outside the atmosphere.

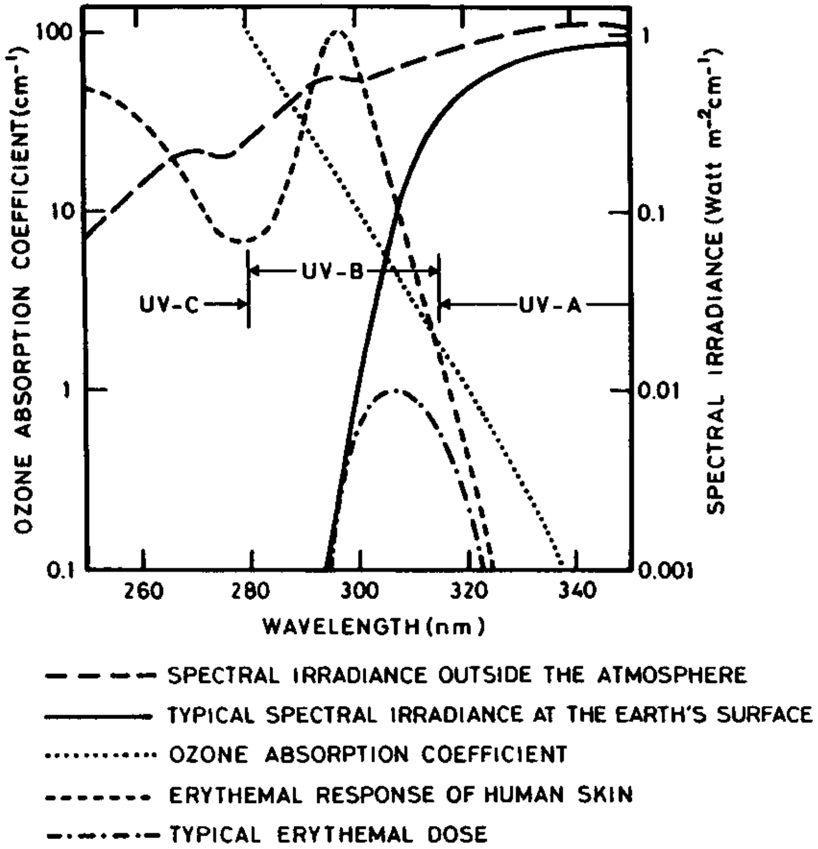

Fig. 2.2. Erythemal action of radiation compared with solar radiation at ground level and ozone spectrum.

The penetration of solar radiation is essentially governed by molecular oxygen and ozone. Molecular oxygen absorbs in several band systems : from 100 to 175 nm : the Schumann-Runge continuum where radiation is already entirely absorbed in the mesosphere, from 175 to 200 nm : the O_2 Schumann-Runge bands, radiation reaches the upper stratosphere and the resulting atomic oxygen produces ozone, from 200 to 242 nm : the weaker Herzberg continuum contributes significantly to radiation absorption in the stratosphere.

Absorption by ozone is important in its Hartley bands between 200 and 310 nm with a maximum around 367 nm, as ozone is distributed mainly in the stratosphere and as the lower wavelength are entirely absorbed at higher altitudes, it is the edge of the Hartley bands which determines the U.V. limit of the solar spectrum received at ground level. Ozone has still a much weaker absorption in the visible, centered around 600 nm which gives it its blue colour : the Chappuis bands.

Visible radiation

The remaining region of the spectrum between 300 and 1000 nm contains about 99% of the total solar energy received at ground level and responsible for photosynthesis and radiative transfer to the atmosphere.

The range of vision, for man and other visally oriented mammals, begins at around 400 nm to end around 650 nm spanning the blue to the red. By night, these frequencies are shifted to the red, up to 700 nm; however, the visible spectrum extends down to 300 nm for insects and other lower animals.

Very few gases absorb significantly in the visible, beside the Chappuis bands of ozone, water vapor NO_2 and SO_2 have weak absorption. The main optical effect is light scattering by molecules and aerosols. Molecules scatter light according to the Rayleigh law :

$$\sigma = \frac{32\,\pi^3\,R}{3N_A\,\lambda^4}\,(n-1)^2\,\frac{T}{p}\,\frac{6+3d}{6-7d}$$

where σ is the scattering cross section, R the perfect gases constant, N_A : the Avogadro number, n : the refractive index of air and d is a depolarisation factor of molecules due to their anisotropy, making this cross section proportional to :

$$\sigma \sim \frac{n}{\lambda^4}\;\frac{T}{p}$$

with a phase function of

$$p(\theta) = \frac{3}{4}\,(1 + \cos^2\theta)$$

and a strong polarization which is total at 90°.
This scattering process is the origin of the blue color of the sky, and, if we could see down to 300 nm, every distant object would be confused in haze.

*

This molecular case is a small particule limit of a more general case : the Mie scattering theory where the parameter $x = \frac{2\pi r}{\lambda}$ becomes close or greater than 1. The Mie theory is marked by a dependancy on wavelength which is less pronounced than the $\frac{1}{\lambda^4}$ dependancy of the Rayleigh scattering and a phase function which has a maximum in the forward direction. Mie scattering of natural light is perceived as white while Rayleigh scattering has a deep blue colour. Mie theory can also be used for absorbing particules with complex refractive index.

Atmospheric aerosols are liquid or solid particles suspended in the air. Tropospheric aerosols originate from ground dust eroded by the winds, industrial pollution, natural fires, sea sprays. Stratospheric aerosols can originate from the direct transport of dust originating from large volcanic explosions; however, they are generally formed in the gas phase by sulfuric gases around condensation nuclei, it is now admitted that they consist of droplets composed of 75% sulfuric acid and 25% H_2O; a layer called the Junge layer is often observed aound 17 km and the total burden of stratospheric aerosols is considerably enhanced after volcanic eruptions leading to an increase of the stratospheric sulfur content. The size of the Junge layer particles is centered around 0.15 - 0.50 µm while the background aerosol consists of much smaller particles (0.05 µm). Finally, in the mesosphere, noctilucent clouds are observed at high lattitudes around the altitude of 80 km and metallic microparticles resulting from the desintegration of meteorites and shooting stars constitute the possible condensation centers for the lower altitude aerosols.

The effects of aerosols on radiative transfer is still much debated, stratospheric aerosol layers, by preventing the solar radiation from reaching the ground would result in tropospheric cooling as examplified by the historical records of the winters of 1784 and 1816 which were influenced by the volcanic explosions of Loki (Iceland) and Tambora (Java). In the troposphere, aerosols could result in a warming by increasing the amount of solar energy deposition and may lead to an increase of the number of condensation nuclei, causing an increase in precipitations.

A renewed interest in the atmospheric effects of aerosols exists since the recent explosions of Mount St Helens in the North Western United State and El Chichon in Southern Mexico in 1980 and 1982. After both events, an increase in sunset colorations was observed worldwide.

Infrared radiation

The infrared spectrum above 1 µm covers only a small portion of the solar energy coming to the earth but it absorbs part of the solar radiation reemitted by the earth with a maximum around 10 µm. The infrared telluric transmittance spectrum is represented on figure 2-3, on sees that the main drives of present radiative transfer are H_2O, CO_2 and O_3; their spectra and effects will be discussed in the next chapter. One of the notable features of figure 2-3 is the presence of atmospheric "windows", of which the most interesting is situated between the O_3

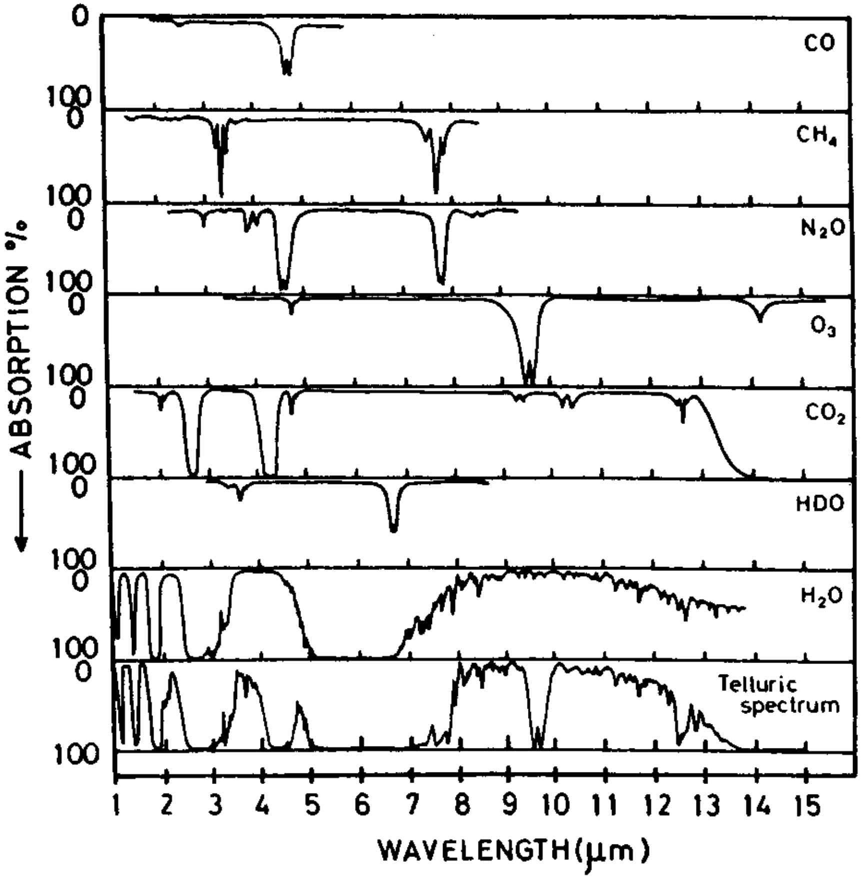

Fig. 2.3. Representation of the telluric infrared transmission spectrum, the atmospheric windows and absorptions of the main gases are clearly represented.

9.6 µm bands and the CO_2 15 µm band, in fact a high resolution study of this region shows numerous absorption lines by stratospheric and tropospheric minor constituents but these still permit a large amount of earth radiation to escape to outer space. Variations in the concentrations of minor gases absorbing in this window, notably the "freons" would lead to a much larger amount of energy trapped in the troposphere. The analogy to the operation of a greenhouse, transparent in the visible and opaque in the I.R. is evident, however, the absorbing gas radiates itself and retransmits energy leading to a much more complicated formalism.

Briefly the radiative transfer equation is a balance equation which can be written a point M and for a direction $\vec{s}$ as :

$$\frac{d\, I(M,\vec{s})}{ds} = - k(M) \{I(M,\vec{s}) - J(M,\vec{s})\}$$

where $I(M,\vec{s})$ is the radiation flux and $J(M,\vec{s})$ is the radiation source and $k(M)$ is the absorption coefficient which is a function of frequency; integrating this equation in the absence of a source in the medium, the familiar Beer-Lambert law of exponential absorption is obtained. The safest way to compute the telluric radiative transfer is by now to integrate the radiative transfer equation line by line, previously different approximations such as band models have been used, they prove themselves to be either too complex for qualitative computation or not elaborate enough for quantitative studies, their accuracy and applicability must be reviewed case by case.

Radiation is only a part of the climate problem which cannot be addressed without involving the entire land-sea-ice system; there is now a widespread disagreement on the evolution of the earth's climate, the CO_2 increase leading to a greenhouse effect while astronomical and thermodynamical considerations lead theoreticians to predict a cooling.

LECTURE 3

INFRARED SPECTROSCOPY AND THE ATMOSPHERE

Introduction

In the infrared region, the atmospheric absorption is mainly due to rotation-vibration bands of molecules. These bands correspond to the transitions between vibrational states and they are divided in lines directly related to the rotational levels of the upper and lower states.

Up to 30 years ago, only few limited lines could be resolved in atmospheric spectra, and atmospheric spectroscopists were happy to identify constituents by broad band signatures. Now, modern instruments resolve most of the lines of small atmospheric molecules and when the molecular parameters are known, all the determination problems can be solved by the study of isolated line features. The radiative transfer followed the same path, evolving from linear and square root approximations to empirical band models and presently to line by line integration. As usual in numerical analysis, in most cases, the near future availability of cheap and ulfrafast computers will terminate all systematic use of band models.

A brief reminder of absorption laws

The transmission of any absorbing medium can be expressed as a function of frequency ν by

$$T(\nu) = \frac{I(\nu)}{I_o(\nu)} = e^{-k(\nu)w} = e^{-\tau(\nu)}$$

where $I(\nu)$ and $I_o(\nu)$ are respectively the luminous intensities of incident and transmitted light, w is called the optical path, $k(\nu)$ is the absorption coefficient and $\tau(\nu)$ is the optical depth. $T(\nu)$ could be considered as the sepctrum observed by a perfect instrument while $k(\nu)$ can be deduced from theoretical considerations using individual line profiles and parameters in the case of a single line :

$$k(\nu) = S\ f(\nu)$$

where $f(\nu)$ is the line profile and S, the "strength" of the line. The parameter usually measured on a spectrum is the absorption :

$$A(\nu) = 1 - T(\nu)$$

which integrated on a feature becomes the integrated absorption or equivalent width, when the absorption is linear :

$$e^{-\tau(\nu)} = 1 - \tau(\nu) \text{ and}$$
$$A(\nu) = \tau(\nu)$$

which combined with the relationship between optical path and concentration :

$$w = n\ell$$

and with the normalisation of $k(\nu)$ gives

$$W = \int_{\nu_1}^{\nu_2} A(\nu) = \int_{\nu_1}^{\nu_2} n\ell\ k(\nu) = S\ n\ell$$

and permits to deduce the concentration.
Unhappily, neither nature nor instruments like the linear cases and much more elaborate computations have to be performed.

Line shape

The line shape is the function which distributes the energy absorbed in the transition; energy conservation gives it the properties of a probability function, essentially normalized to one and centered on the line position.

In the perfect theoretical case of a transition between two states of infinite life time without any perturbations, it should be a Dirac distribution but this case is never observed in the infrared, the life time of the stable upper states of rotational vibrational transitions being close to 10^{-2} sec, the natural line width predicted by the uncertainty principle is lower then 10^{-6} cm^{-1}. This effect could become more important in the case of electronic transitions where the life time of the states is much shorter and when the upper state leads to the dissociation of the molecule, the broadening becomes so wide that is smears all molecular structure.

In the infrared the main broadening effect will be the pressure effect when collisions between molecules interrupt the oscillation of the molecular dipole moment, this corresponds to the addition of a random phase and this line shape expresses itself by

$$f(\nu) = \frac{\alpha_L}{\pi[(\nu-\nu_o)^2 + \alpha_L^2]}$$

where ν_o is the center of the line, α_L is called the Lorentz line width and corresponds to the half width of the line at half height. The dependancy of α_L on pressure and temperature expresses itself by

$$\alpha_L(T) = \alpha_L(T_o)\left(\frac{P}{P_o}\right)^m\left(\frac{T_o}{T}\right)^n$$

where P and T are respectively pressure and temperature. Collision theory predicts values of $m = 1$ and $n = 0.5$, experimental determinations tend to yield values of m slightly lower than 1 and values of n between 0.5 and 1. This is related to the nonapplication of the theory of elastic collisions to real molecules.

Departure from the Lorentz profile are observed in the far wings which are significant at high pressures, in the case of tropospheric H_2O absorption, this leads to a current conflict on the nature of the H_2O continuum which is attributed either to the distant wings of lines or to a broad absorption by a water vapor dimer or polymer.

Another important phenomenon for the broadening of lines is the Doppler effect which results from the randon trajectories of molecules in the optical path giving for each molecule a frequency shift of

$$\Delta\nu = \frac{v}{c}\ \nu_o$$

where v is the speed of the molecule, translated to a molecule population, it leads to the following profile :

$$f(\nu) = \frac{1}{2\sqrt{\pi}} \quad \exp\left| - \left(\frac{\nu - \nu_o}{\alpha_D} \right) \right|$$

where α_D is the Dopplerian half-width and ν_o the frequency at the line center and its expression is :

$$\alpha_D = \frac{\nu_o}{c} \left(\frac{2\ k\ T}{m} \right)^{1/2}$$

where m is the mass of the molecule.

The variation of these widths with altitude are shown in figure 3.1 for the case of two NO_2 line, the troposphere is clearly Lorentzian while in the stratosphere and above the Doppler profile cannot be neglected any more, and a Voigt profile has to be used :

$$f(\nu) = \frac{k_o y}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)\ dt}{y^2 + (x-t)^2}$$

where $$k_o = \frac{1}{\alpha} \left(\frac{\ln 2}{\pi} \right)^{0.5}$$

$$y = \frac{1}{\alpha_D} (\ln 2)^{0.5}$$

$$x = \frac{\nu - \nu_o}{\alpha_D} \quad (\ln 2)^{0.5}$$

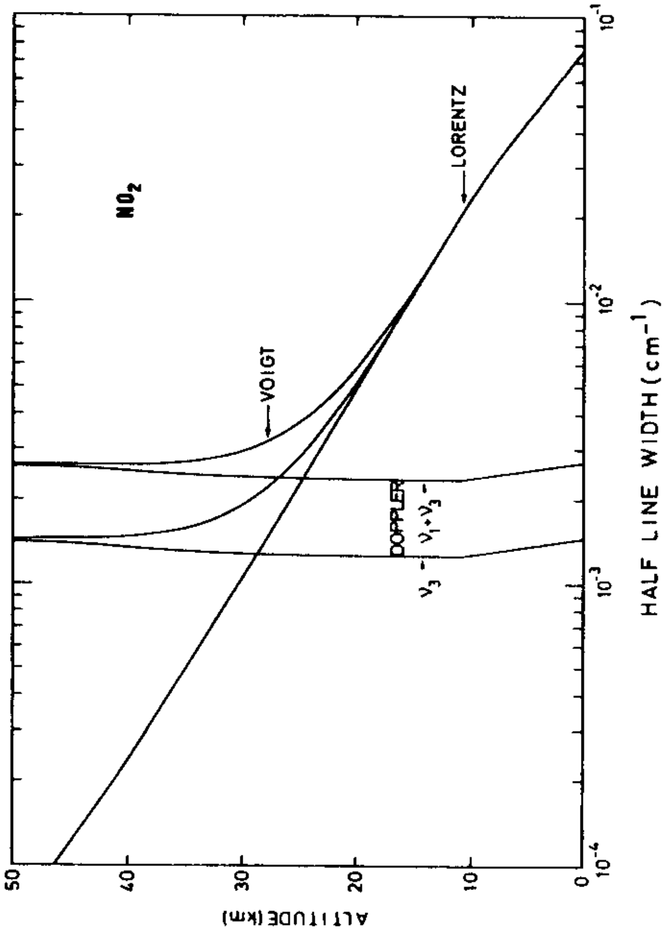

Fig. 3.1. NO_2 line width as a function of altitude for the ν_3 (1600 cm^{-1}) and $\nu_1 + \nu_3$ (2900 cm^{-1}) bands.

This non analytical integral is the real part of the complex probability function and in recent years, many analytical approximations and algorithms have been developed to evaluate it. The most recent exact techniques being surprisingly faster than the older analytical approaches. The three profiles are compared in figure 3.2 where the saturation phenomenon is illustrated; when the line intensity increases, the total echanged energy does not increase linearly anymore and the Doppler line even becomes a square function and absorbs independantly of the optical path. The relation between equivalent width and integrated absorption is called the curve of growth and its two extreme cases are called linear and saturated.

Line parameters

Four parameters permit most of the spectral synthesis : the line strength : S, the lorentzian half width : α_L, the energy of the lower level of the transition : E and the central frequency of the line : ν_o. The energy E is necessary because it permits to compute the intensity variation as a function of temperature by the expression

$$S(T) = S_o\left(\frac{T_o}{T}\right)^n \exp - \left[\frac{hc\ E(T_o - T)}{k\ T.T_o}\right]$$

the exponent n is equal to 1. for diatomic and linear molecules and equal to 1.5 for asymmetrical and symmetrical tops.

These parameters are determined from the molecular quantum numbers and coefficients fitted to reproduce laboratory spectra. Most of the necessary data for atmospheric molecules is now included in two compilations the AFGL data tape and the French GEISA tape, both are similar in use, the GEISA tape includes sometime more molecules and newer data. Both works are a cooperative effort with insistance on quality and consistency.

The mocules of the AFGL data tape are H_2O, CO_2, O_3, N_2O, CO, CH_4, O_2, NO, SO_2, NO_2, NH_3, HNO_3, OH, HF, HCl, HBr, HI, ClO, OCS, CH_2O.

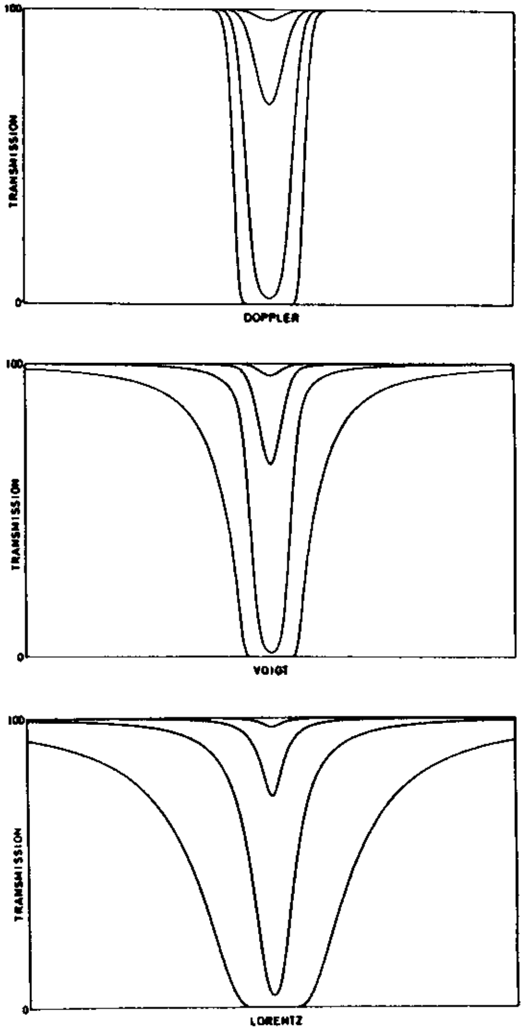

Fig. 3.2. Comparison between the Lorentz, Doppler and Voigt profiles, the optical path being multiplied each time by a factor of 10.

Other molecules will be included in later versions. These data sets are designed for use at middle atmospheric temperatures, currently new data sets are being elaborated for the study of flame spectroscopy and other high temperature applications.

Individual molecules in the atmosphere

The rotation vibration spectra of H_2O, CO_2, N_2O, CH_4, CO and O_3 have already been introduced by Pr. Amat, they will be reviewed here only for their relevance to radiative transfer and molecular concentration determination

H_2O asymmetric top molecule with several bands extending on most of the infrared spectrum, the lines seem to be randomly arranged, its main absorption bands are around 2.7 µm and 6.3 µm; due to the importance of its tropospheric concentration and its presence up to 80 km, H_2O is an important component of all radiation exchange.

CO_2 linear molecule with regularly spaced lines, CO_2, is mixed in the homosphere at around 330 ppm, it has intense absorptions in its 15 µm and 4.3 µm bands, its slow yearly increase could lead to a doubling in about 100 year if the present rate of increase is sustained. It presents also the interest of being observable up to the altitude of 130 km by infrared absorption spectroscopy.

N_2O linear molecule with two important atmospheric bands at 7.8 µm and 4.5 µm; its spectrum is very similar to CO_2; there are speculations that the use of fertilizers leads to an N_2O increase, however its mixing ratio of 3 ppm seems to have remained invariant for the last 30 years.

CH_4 spherical top molecule with its main bands at 3.3 µm and 7.6 µm. These bands consist of regularly spaced strong manifolds separated by weaker lines. The determination of CH_4 is important for the determination of vertical transport in the stratosphere, also, as in the N_2O case, a CH_4 increase is suspected to be associated with the intensification of agricultural activity.

CO diatomic molecule, its fundamental band lies at 4.7 µm; CO has little influence on radiative transfer, its atmospheric interest is that of a major tropospheric pollution tracer and at higher altitudes as the final product of CO_2 photodissociation and methane oxidation. Its telluric spectrum is contaminated by solar chromospheric lines.

O_3 a symmetric top molecule with well defined bands of extremely complex structure. Its main band both for teledetection and radiative transfer applications is the 9.6 µm ν_3 band.

NO, OH and ClO : these diatomic molecules are technically free radicals, they present an incomplete orbital shell which make their fundamental states spin doublets with well separated components. In the NO case, the fundamental band lies at 5.3 µm and is a combination of four subbands presenting each a combination of P, Q and R branches. These infrared parameters are important for the determination of NO concentrations, NO has no influence in the radiative transfer of the middle atmosphere, however near the altitude of 140 km, it could play a role in the radiative cooling of the thermosphere. The OH and ClO atmospheric observations in the infrared have not yet been performed despite their photochemical importance.

NO_2 asymmetric top molecule very close to a prolate symmetric top with a weak spin splitting effect. Its most important absorption is its ν_3 band at 6.25 µm.

HCl, HF, HBr and HI : these are simple diatomic molecules, accurate line positions are necessary to distinguish their absorptions from those of contaminating lines.

HNO_3 and freons ($CFCl_3$ and CF_2Cl_2) : these complex molecules have absorptions in several spectral regions, the most interesting for their determination being the 12 μm atmospheric window. Nitric acid is an asymmetric top with several resonant bands exchanging energy between each other, after years of theoretical efforts by several groups, valid line parameters are now implemented on the data tapes. The freons are an even more complex case, even at infinite resolution, no single line can be identified and one is left only with laboratory studies of band intensity for quantitative determinations; the freons, absent from the spectrum in 1965 are now an important component of radiative transfer in the 12 μm region.

LECTURE 4

OBSERVATION TECHNIQUES

This lecture will deal with observation techniques involving spectral analysis which is the case of all remote sensing techniques and of a few in-situ techniques. Observations of atmospheric composition and properties using mass spectrometry, electron capture or chemical analysis of samples will not be covered here, they are however often a necessary verification of optical techniques.

Observation geometries

Spectrometry can be divided in two classes : absorption and emission. In the U.V., visible and infrared, the signal from the sun is still much stronger than the atmospheric emission; in the visible and the near infrared, reflected sunlight by the moon, by the planet Venus or star lights could also be used as sources while in the middle infrared, the moon begins to be comparable with atmospheric emissions. In the microwave pure rotation spectrum, atmospheric emission dominates and absorption spectroscopy is no longer possible.

Absorption spectrometry can be performed from the ground, balloon, airplane or from space.

As spectral properties vary with altitude, it is convenient to layer the atmosphere, using pressure steps in order to have a similar number of molecules in each layer. For a solar zenith distance χ, this gives :

$$\tau = \sec \chi \sum_{i=i}^{m} \tau_i = \sec \chi \sum_{i=1}^{m} n_i \, k_i \, \ell_i$$

k, n and ℓ are defined each for layer i. This approximation implies that the earth is flat, when the solar zenith angle becomes greater than 85°, it ceases to be correct and earth sphericity must be taken into account. This used to be done by using approximation functions, now, as in many other computations, it is preferable and easier to resort to exact calculation. In the case where atmospheric refraction becomes important, the evaluation of τ must be combined with a ray tracing program.

Use of horizontal paths enhances the geometric length of the optical path by a factor of about 30, thus for detection of minor species, the best site will be a station where sunset or sunrise can be observed below the horizon. Many existing mountain observatories satisfy this condition and have also the advantadge of being in high dry sites, far from the sources of industrial pollution and often well above the winter clouds.

Airborne and balloon instruments permit the same investigations above the horizon but their highest effeciency is obtained by pointing at zenith angles greater than 90°, this technique is called limb sounding. The zone of greater absorption is the altitude where the ray is closest to the earth, this permits a scan of altitudes as the sun rises or sets; figure 4.1 illustrates limb-sounding.

On the ground and in the air, long path spectrometry can be also achieved by using a source and a detector at a sufficient distance or by operating a reflecting cell, this technique is difficult and few successfull applications have been published.

In space, the instrumental possibilities have been until now very limited because of spececrafts size, power and availability of space platforms for atmospheric science. However, the results obtained from the few missions to have flown lead to believe that space will be the site of the main atmospheric observatories when large permanent stations will permit the evaluation and check out of new instruments and when the cost of orbit access will decrease. From space two geometries are possible : limb sounding spectrometry and nadir sounding. Nadir sounding uses atmospheric thermal emission as a source, absorption of back

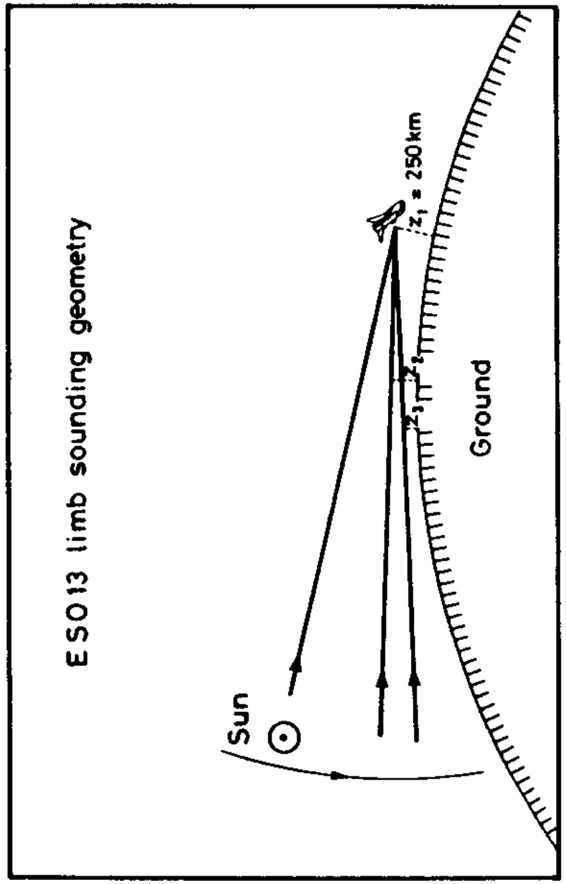

Fig. 4.1. Limb sounding geometry in the case of the Spacelab borne ES013 grille spectrometer.

scattered U.V. radiation or airglow. Airglow measurements of the U.V. bands of nitric oxide from rockets or satellites have already been for 20 years one of its prime measurement techniques in the mesosphere.

Inversion of data

The inversion and interpretation techniques of remote sensing data still vary from case to case. In the case of limb sounding, one can assume that successive layers are scanned and in which each time, a new integrated absorption or "equivalent width" W is measured between frequencies ν_1 and ν_2; the successive equation are :

$$F(n_1) = W_1 - \int_{\nu_1}^{\nu_2} [1 - e^{-k_1(\nu)\, n_1\, \ell_1}]\, d\ = 0$$

$$F(n_2) = W_2 - \int_{\nu_1}^{\nu_2} [1 - e^{-k_1(\nu)\, n_1 \ell_1' - k_2(\nu)\, n_2 \ell_2}] = 0$$

$$F(n_m) = W_m - \int_{\nu_1}^{\nu_2} [\ 1 - e^{-\sum_{i=1}^{m} k_i(\nu)\, n_i\, \ell_i^{m-i}}\ ] = 0$$

where m is the index of each layer varying from the value 1 corresponding to the higher layer up to the value corresponding to the lower layer.

The solution of this non linear triangular system gives the concentrations as a function of altitude and the problem encountered are those of numerical analysis, in the absence of noise, the Newton-Raphson process :

$$n_j^{i+1} = n_j^i - \frac{F(n_j^i)}{F'(n_j^i)}$$

seems attractive, however random errors may propagate oscillations through the system; this inversion technique from top to bottom, is usually called onion peeling. The stability of the inversion process is enhanced by the extremely specific weighting function of limb sounding which gives 75% of the total absorption in a 2 km layer above the grazing ray altitude; however, in the few cases where a constituent

increases with altitude this is no longer true and the technique could oscillate; where possible, the obtained result should be checked by simulating the observation in order to see which range of concentrations leads to results which cannot be distinguished from the observation and these define the experimental error bars. In the case of ground or nadir sounding the equation system is no longer triangular and the number of equations seems always smaller than the number of physical quantities to be determined. From space, a frequently used technique is to indroduce several spectral filters which correspond to emissions arising from very specific atmospheric levels and by attributing them the proper weighting functions, to obtain the vertical destribution of the studied property putting all data in agreement by a relaxation process; this method is called the Chahine technique and has been successful in the determination of temperatures from satellite.

Other techniques make hypotheses on the wanted result and make them evolve until they fit the observed data sets; in limited cases, concerned with specific applications, the physics of the problem is forgotten and parameters are adjusted to express a relation between satellite data and ground truth and when this is established, it is extrapolated worldwide.

Instrumental requirements

The properties of instruments depend on their scientific aim, optical instruments could be categorized by several parameters :

- resolution
- sensitivity
- field of view
- speed of data acquisition
- imaging capability
- availability

Interferometers and even automatized scanning spectrometers present the advantadge of being multipurpose instruments and permit to investigate together several atmospheric properties and constituents.

Several hundreds of instruments have been used for atmospheric studies in recent years, this course will detail only a few. Among them : the Dobson instrument which is a spectrophotometer based on the comparison between wavelengths pairs and which is still the primary ozone instrument and as an example of space instrument : the belgo-french spacelab grille spectrometer.

REFERENCES

I will assist any participant in researching a particular subject, the inflation of references on items of atmospheric relevance is colossal, for example the keyword "line shape" gives more than 10000 references in the INSPEC recension for the last 15 years. I will very subjectively refer these books as the beginning of an atmospheric science library :

Banks, P.M. and Kockarts, G., Aeronomy, Academic Press, New York, 1973.

Brasseur, G. and Solomon, S., Aeronomy of the middle atmosphere, Reidel, Dordrecht, 1984.

Goody, R.M., Atmospheric radiation, theoretical basis, Clarendon Press, Oxford, 1964.

Houghton, J.T., The physics of atmospheres, Cambridge University press, 1977.

Kerker, M., The scattering of light, Academic Press, New York (1969).

Kontratyev, J.Y., Radiation in the atmosphere, Academic Press, New-York (1970).

Twomey, S., Atmospheric aerosols, Elsevier, Amsterdam (1977).

Zuev, V.E., Atmospheric transparency in the visible and the infrared, I.P.S.T., Jerusalem (1970); translated from the Russian original (Moscow, 1966).

For the problem of anthropogenic perturbations on ozone, one of the latest paper to have appeared is :

Prather, M.J., McElroy, M.B., Wofsy, M.C. : Reductions in ozone at high concentrations of stratospheric halogens, Nature, 312, 227-231 (1984).