Vietnam Journal of Earth Sciences, 41(2), 138–155, Doi: 10.15625/0866-7187/41/2/13724

(VAST)

Vietnam Academy of Science and Technology

Vietnam Journal of Earth Sciences

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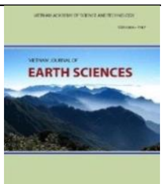

The first Vietnam School of Earth Observation: Atmospheric Remote Sensing and Molecular Spectroscopy

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Received 29 December 2018; Received in revised form 8 March 2019; Accepted 29 March 2019

ABSTRACT

In this review paper, we give an introduction to molecular spectroscopy and its relation to atmospheric remote sensing and examples of recent developments in spectroscopic experimental techniques and modelling. Atmospheric retrieval techniques, based on radiative transfer theories and molecular spectroscopy as well as some atmospheric remote sensing missions using spectroscopic techniques are presented.

Keywords: Molecular spectroscopy; atmospheric remote sensing; radiative transfer.

1. Introduction

Climate change and air pollution are among the most serious problems presently facing mankind. Primary pollutants like nitrogen oxides, volatile organics, and fine particles as well as secondary pollutants formed subsequently in the gas phase, such as ozone, are a major problem for public health, especially in urban areas. It is also well established that the chemical composition of the atmosphere is a main factor which affects the Earth's climate and that climate change is largely due to the presence of greenhouse gases (GHG) whose mixing ratios significantly increased since preindustrial time. Various instruments, including spectrometers and LIDAR, on-board satellites, balloons, aircrafts and in ground-based observatories are used

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for remote sensing of atmospheric trace gases and aerosols in order to determine spatial and seasonal variations of atmospheric species and to understand the causes and consequences of global warming. They measure the solar radiation transmitted through the atmosphere, radiation emitted by the ground, and radiation emitted by the atmosphere itself as a function of the wavelength. Inversion methods are used to analyze atmospheric spectra. They use accurate spectroscopic parameters of individu molecules from laboratory experiments and theory as well as radiative transfer codes. Applications such as gas/aerosols retrievals with satellites, studies of urban pollution, GHG detection and climate change studies rely on precise and accurate atmospheric measurements. The most advanced spectroscopic remote sensing techniques are needed to meet the requirements of 3D atmospheric chemistry-transport models used for prediction of the concentrations of air pollutants and GHG.

The first Vietnam School of Earth Observation (VSEO)[†] discussed recent advances in atmospheric remote sensing made possible through accurate measurement, understanding and interpretation of molecular spectra. The aim of this school was to provide to all participants a multidisciplinary training (lectures, tutorials, conferences) of this important subdiscipline of the atmospheric sciences. This review paper summarizes all the topics discussed during this first VSEO. In the first part of this paper, we give a general introduction to molecular spectroscopy and its relation to remote sensing (section 1) followed by a review of advanced experimental spectroscopic techniques (section 2). Spectra modelling including the effects of collisions on the spectral shapes and their consequences for atmospheric remote sensing are then presented in section 3. In the second part of this paper, an introduction to atmospheric radiative transfer and atmospheric retrieval is given (section 4). It is followed by the presentation of a state-of-the art ground-based high resolution infrared observatory for precise atmospheric measurements and monitoring of atmospheric pollutants and GHG (section 5). Finally, we present various atmospheric remote sensing missions using spectroscopic techniques (section 6).

2. Molecular spectroscopy and its relation to remote sensing

Spectroscopy is an important subdiscipline of chemical physics treated in detail in many chemistry and physics text books. It studies the interaction of electromagnetic radiation with matter, as a function of the wavelength of the radiation. In chemical physics, molecular spectroscopy is used to determine the internal structure of molecules, their interactions with each other as well as the related dynamics. In the geophysical sciences, it is used to study the various remote objects of the Universe by analyzing the radiation they emit and absorb with spectroscopic observatories (ground or space-based). The Earth's atmosphere, as well as any other planetary atmosphere in the solar system or beyond, is considered to be a diluted medium. The atmospheric species that it contains can thus in principal be treated as isolated, however, collisions have to be considered as we will discuss below. The atmospheric species include aerosol particles, molecules and atoms. In this paper we focus on molecular spectroscopy used for remote sensing of molecules. We note that spectroscopic instruments are also extensively used for so-called "*in-situ*" measurements. Here, the instruments are themselves embedded in the medium to be studied. We also mention the use of spectroscopic techniques in simulation chambers where

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[†] The first Vietnam School of Earth Observation was held at International Centre for Interdisciplinary Science and Education in Quy Nhon from August 26-31, 2018

physico-chemical processes of the atmosphere are studied.

Earth receives radiation mainly from the sun, in the ultraviolet, visible and near-infrared spectral region. It also acts itself as a black body and emits radiation (partly) back to space, mainly in the infrared spectral region. The received and emitted radiation travels through the various atmospheric layers where it is scattered and absorbed by the different species. For remote sensing of molecules in the Earth atmosphere, the whole infrared domain (far, mid and near IR) is of particular importance since specific molecular fingerprints lie in this domain. In principal, electronic spectroscopy using ultraviolet and visible electromagnetic radiation can also be used for remote sensing as long as the radiation is not completely attenuated (as it is the case, for example, in the lower, dense layers of the atmosphere) and as long the optical transitions are specific enough to recognize particular molecules. Pure rotational spectroscopy, in the microwave spectral region, can be used for remote sensing purposes too as long as the spectral lines are well separated and not congested by collisional broadening (which is the case in the lower atmosphere).

Infrared radiation excites rotational and vibrational motions inside molecules who possess 3N-3 degrees of freedom to store energy internally after absorption (with N being the number of atoms of the molecule). The frequency positions of the thousands of rovibrational absorption lines, their intensities as well as their line shape parameters have to be measured in the laboratory or calculated, for example, by ab-initio quantum chemistry. All together they form what we call “spectroscopic parameters” which are listed in international databases (see Fig. 1). Very often, a synergy between theory and laboratory experiments permits extrapolation of these parameters to temperature and pressure domains difficult to cover by the experiment. This is shown in the upper right part of Fig. 1 who gives a general strategic scheme for atmospheric remote sensing using molecular spectroscopy. Many of the spectroscopic parameters (e.g. intensities) exhibit a strong temperature dependence.

Note that databases, in the center of Fig. 1, usually have to be updated constantly since the precision demands of remote sensing missions are constantly rising. For a database like HITRAN (Gordon et al., 2017) bi-annual conferences are held where atmospheric scientists and spectroscopists interact in order to discuss how to increase accuracies, complete data sets or to include new, more significant parameters. One can even say that remote sensing of objects of the Universe is one of the main driving force for the development of a database like HITRAN. The scientists working on “real world spectra” will use the databases for spectral analysis and retrieval of mixing ratio profiles of relevant molecules. This process is called “inversion” and will be depicted below. In order to fully exploit the remote sensing measurement, every single feature of the atmospheric spectrum is simulated in the inversion process by minimizing the residuals obtained after an “observed-calculated” subtraction. Spectral structures in the residuals, above noise level, often reveal new molecules or spectroscopic parameters that are not known with sufficient precision.

Once an atmospheric profile of a particular molecule has been determined in this way, the results are transferred to scientists running physico-chemical models of the Earth’s atmosphere (cf. lower left part of Fig. 1). The remote sensing results are used as strong constraints in the modeling process. The interaction between atmospheric chemistry and remote sensing scientists should be as strong as possible since atmospheric models need constraints to be run. On the other hand, these models make predictions of atmospheric molecules and thus are able to suggest new, more relevant observations of key species.

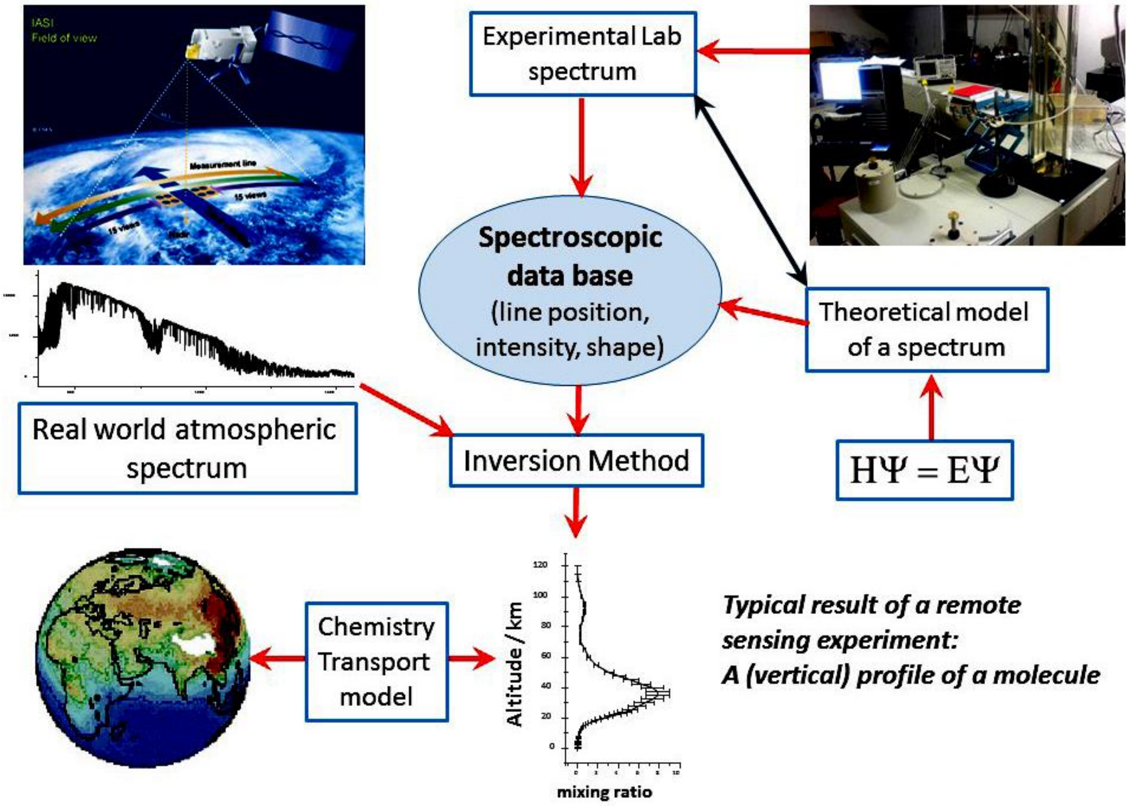

Figure 1. Strategic scheme of remote sensing of molecules in the Earth's atmospher

3. Advanced experimental spectroscopic techniques

High resolution molecular spectroscopy is continuously redefined by new experimental and theoretical possibilities. From the experimental point of view, scientists in specialized laboratories continuously explore innovative technological solutions to develop performing spectrometers by removing a number of technological barriers. By working in parallel on the three central elements of a spectroscopy experiment, namely: the source, the environment sample and the detection, they worked mainly on five axes of requirement and improvement to obtain high-performance spectrometers in the context of gas phase spectroscopic analyses: (i) the spectral coverage and the continuous tunability, (ii) the frequency and time resolutions, (iii) the detection limits (iv) the frequency metrology and (v) the usability, compactness and robustness of the instruments. On these five axes of progress, depend the capability to (a) improve the molecular parameters in spectroscopic databases, (b) to study new gas phase atmospheric compounds at trace level and c) to transfer laboratory measurements towards atmospheric monitoring in realistic conditions.

Since an exhaustive overview was not possible during the limited time of VSEO, a focus was laid on advanced spectroscopic techniques, using electronic, optoelectronic and optical sources for the detection and the quantification of atmospheric molecular species from the microwave to the far-IR spectral domain. High-resolution rotational spectroscopy using electronic sources was presented in a first lecture with an overview of the different radiation sources and detectors. Some examples of room temperature rotational absorption frequency measurements using a versatile sub-Terahertz (THz) spectrometer dedicated for trace gas analysis (Mouret et al., 2013) were given highlighting the capability of these instruments to study high-resolution molecular spectra with a huge density of rotational lines. As shown in Fig. 2, this type of spectrometer allowed to study industrial pollutants such as thionyl chloride (Martin-Drumel et al., 2016) or biogenic precursors of secondary organic aerosols in the atmosphere such as methoxyphenols (Roucou et al., 2018). A specific tutorial aiming to assign 2-methoxyphenol millimeter-wave spectrum was proposed to handle some spectroscopic analysis programs commonly used in the international community. Emission rotational spectroscopy were also addressed with the molecular beam Fourier Transform Micro-Wave spectroscopy (Zhakarenko et al., 2016) and the recently developed Chirped Pulse technique (Hindle et al., 2017).

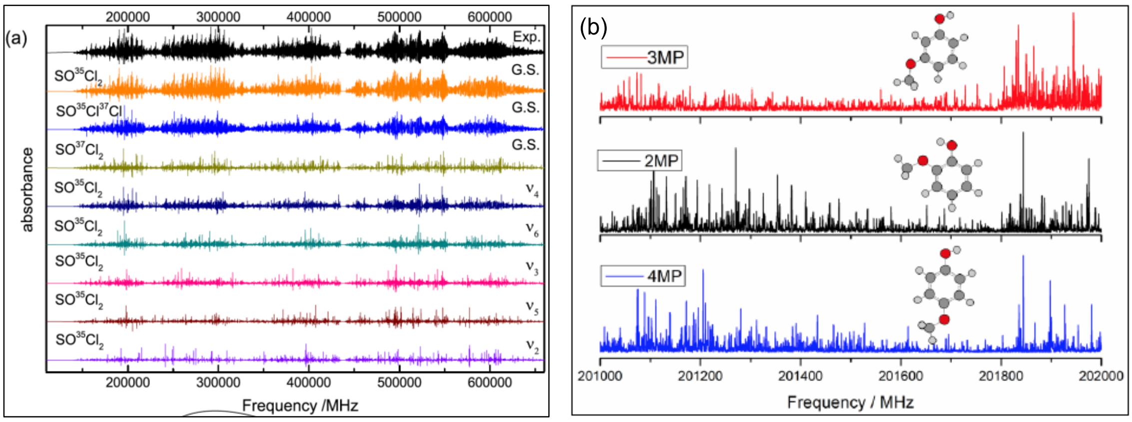

Figure 2. Left: Experimental submillimeter spectrum of thionyl chloride (in black) and all the experimental individual contributions considered in the analysis (in color) [see (Roucou et al., 2017)]. Right: the experimental rotational spectra of the meta (red), ortho (black) and para (blue) isomers of methoxyphenol measured with a Chirped Pulse millimeter-wave spectrometer (Hindle et al., 2017)

In a second lecture, the laser technology was introduced dealing with high-resolution spectroscopy using optoelectronic sources. The principle of a continuous-wave THz spectroscopy by photomixing was described. With an improved sensitivity by means of a propagation in a multipass cell and a unique frequency metrology technique based on femtosecond laser frequency comb, the THz rotational spectra of major atmospheric compounds have been measured and analyzed with this spectrometer. Stable (H_2CO, CH_4, CH_3D, CH_3Cl, ...) and unstable compounds (OH, SH, SO…) have been measured (Bray et al., 2017a,b, Martin-Drumel et al., 2012). Among the spectroscopic applications, precise measurements of pure rotational high J line profiles have been performed allowing for the determination of new spectroscopic parameters or the improvement of previous data included in international spectroscopic databases such as HITRAN. As example, Fig. 3 presented rotational lines of methane measured with an unprecedented degree of accuracy (Bray et al., 2017a) and the correction of the tabulated line intensities of CH_3D (Bray et al., 2017b). All these examples highlight how technological progress in laboratory spectroscopy can allow to improve the atmospheric databases and, therefore, the monitoring of key atmospheric species.

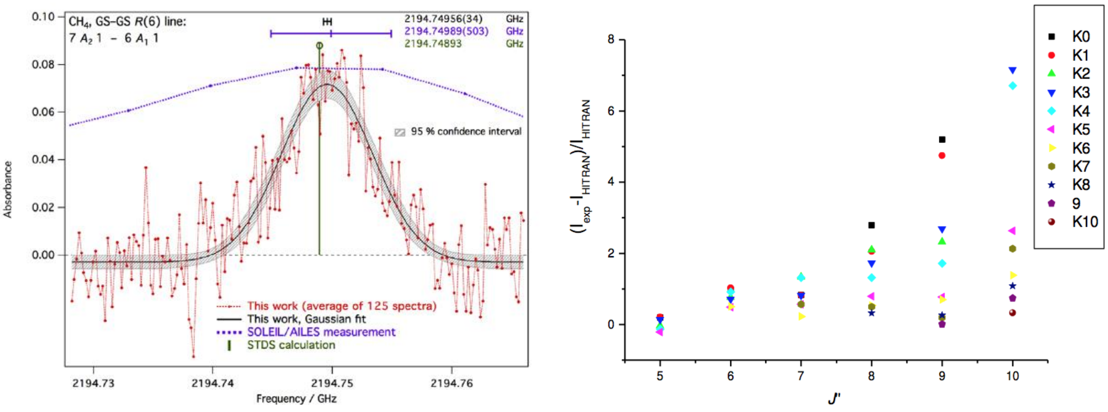

Figure 3. Left: Example of a rotational line of methane measured by a cw-THz synthesizer based on a frequency comb (in black) compared with a high resolution FTIR measurement (blue) [see (Bray et al., 2017)]. Right: Relative difference between experimental CH_3D rotational transition intensities measured with the cw-THz synthesizer and values tabulated in the HITRAN2012 database [see (Bray et al., 2017b)]

4. Collisional effects on spectral shapes and consequences for atmospheric remote sensing

From atmospheric spectra measured by a space-born or ground-based instrument, various properties and species of the sounded atmosphere can be inferred. This retrieval procedure is generally based on the minimization of the difference between the measured spectra and those computed using a forward model, the inferred quantities such as the mixing ratios of the atmospheric species being adjusted. Accurate spectroscopic characterization of the various gas species absorbing in the atmosphere is thus needed for a precise forward calculation and retrieval. For each line of a relevant molecule one needs to know its position, its integrated intensity, the energy of its lower level as well as its line shape in order to compute the spectrum of an absorption transition. The latter is a very important parameter for atmospheric remote sensing since it reflects the pressure (thus atmospheric altitude) dependence of the spectral signature.

For years, the Voigt profile (VP) has been used to model the spectral line shape. It is a convolution of a Gaussian and a Lorentzian profile, respectively describing the Doppler broadening (due to thermal motion of the molecules) and the collisional (pressure) broadening. At high pressure (low altitude), collisional broadening is dominant and the VP is close to a Lorentz function. At low pressure (high altitude), collisional broadening being negligible, only the Doppler effect contributes to the line shape. However, the VP is an over-simplified model which leads to large deviation with respect to the measured spectra (up to several percent, see (Hartmann et al., 2018) and references therein). It is now widely known that accurate line-shape modeling is essential to meet the precision requirements of laboratory measurements and atmospheric remote sensing (see (Hartmann et al., 2018) and references therein).

The Hartmann-Tran (HT) profile overcomes these shortcomings and has been recently recommended by the international union for pure applied chemistry (IUPAC) for applications in high-resolution spectroscopy (Ngo et al., 2012, Tennyson et al., 2014). This profile takes into account various processes affecting the spectral shapes, which were neglected by the VP. The first one is the velocity changes due to intermolecular collisions, also known as the Dicke narrowing effect (Dicke 1953). The second effect is the molecular speed dependences of the individual line broadening and pressure-shifting (Berman 1972). This spectral line shape also accounts for the collisional interferences between transitions (i.e. collisional line-mixing, see Fig. 5). Several studies showed that the HT profile can represent measured spectra of various molecular systems within a few 0.1%, under wide pressure and temperature conditions as well as for various spectral ranges (see Fig. 4 and (Hartmann et al., 2018) and references therein, for instance). This profile is now adopted by spectroscopic databases (e.g. 1]) and also in the spectroscopis and atmospheric remote sensing communities. Note that even limited to the most important atmospheric molecules such as H_2O, CO_2, CH_4 and O_2, providing the HT line-shape parameters for thousands and thousands of lines for atmospheric temperature and pressure condition represent a huge experimental and analysis effort.

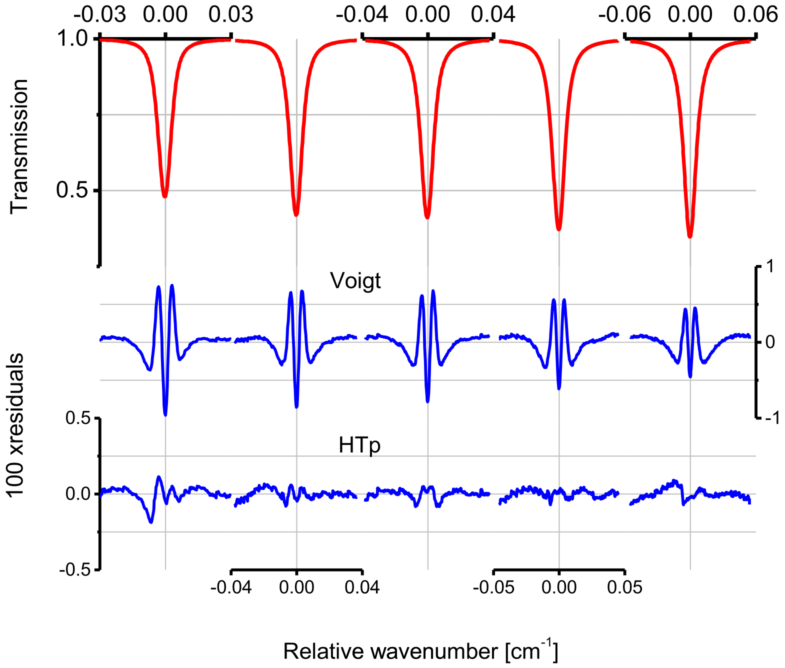

Figure 4. Measured transmission spectra of a CH_4 line broadened by N_2 at room temperature and for various pressures; from left to right: P = 28.26, 43.77, 45.49, 60.88 and 78.86 mbar. The corresponding residuals obtained from fits of these spectra with the Voigt and the HT profiles are represented in the lower panels [see also (Le et al., 2016)]

Figure 5 shows an example of the influence of the line shape, here of the collisional line-mixing, on the retrieval of atmopheric CO_2. Currently, various satellite-based observatories aim to accuratly monitor the carbon dioxide mixing ratio [e.g. (GOSAT, OCO-2, MicroCarb)] since this gas is the most important anthropogenic GHG in our atmosphere. Thanks to their spectral charateristics, the 2.1 and 1.6 μm spectral regions are chosen by these observatories for CO_2 retrieval. The objective is to identify the regional sources and sinks of CO_2 with a precision better than 1%. This puts very severe constraints on the quality of the spectroscopic data and forward spectral models used for CO_2 (Miller et al., 2005, Miller et al., 2007). The example of Fig. 5 [see also (Hartmann et al., 2009)] shows that neglecting collisional line-mixing in a forward model leads to large deviations between the measured and adjusted spectra and therefore to erroneous CO_2 retrievals.

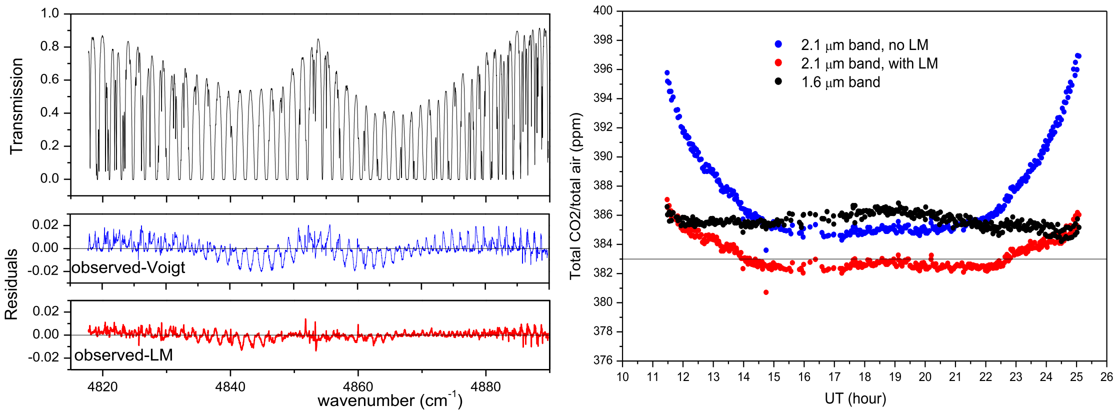

Figure 5. Left: Ground-based atmospheric measurement in the 2.1 μm spectral region (top panel) using a Fourier transform spectrometer, and residuals obtained from fits of this spectrum using the Voigt profile (blue) and using a model taking collisional line-mixing (LM) effect into account (red). In the right panel is the corresponding CO_2 amount retrieved versus the Universal Time of the measurement, obtained with (blue) and without (red) the inclusion of line-mixing in the forward model. The black points are results obtained in the 1.6 μm spectral region

5. Introduction to atmospheric radiative transfer and retrieval

In general, the signal measured by an optical sensor cannot be directly translated into an atmospheric parameter. For each instrument, it is necessary to develop an algorithm allowing to infer target parameters (e.g. vertical profiles of temperature or gas concentrations) from spectral measurements (radiances). To distinguish the principal algorithm classes used, the term of retrieval method, or inverse model, is usually used. In all cases, it is necessary to solve the direct problem: to have an algorithm allowing to simulate/calculate the signal that should be received by the instrument for a given state of the atmosphere and for a given observation geometry. The influence of the instrument function should be accurately modeled for a reliable forward calculation. As an example, Fig. 6 shows how a given instrument impacts the measured signal, here in the case of the IASI nadir looking infrared sounder (Clerbaux et al., 2009).

Atmospheric radiative transfer is a very broad topic covered by numbers of books or scientific papers [e.g. (Goody and Yung 1996, Liou 2002, Stamnes et al., 2017)]. Radiative transfer is mainly based on the electromagnetic wave description of light. The different modeling approaches lead to different results in terms of accuracy and computer time. For example, when scattering is taken into account, Monte Carlo based approaches tend to give very accurate results, but with prohibitive calculation time. Atmosphere radiative codes are usually divided into two families: (1) Line-by-line codes: they calculate the contribution of all atmosphere gases, for each spectral point, (2) Band transmission models where gas transmittance is defined as a mean value per spectral band. A list of examples is given in (Grau and Gastellu-Etchegorry 2013), for instance.

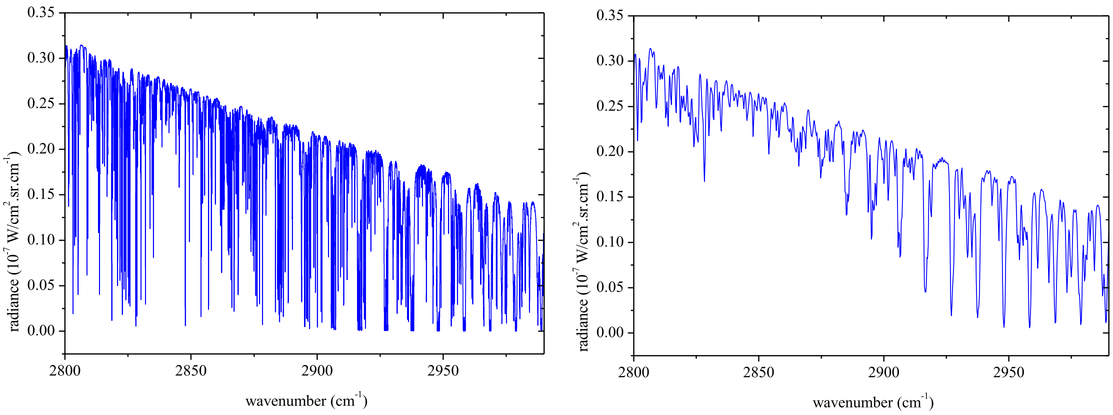

Figure 6. Atmospheric spectra calculated at infinite spectral resolution (left) and equivalent spectra measured by the nadir sounder instrument IASI (right)

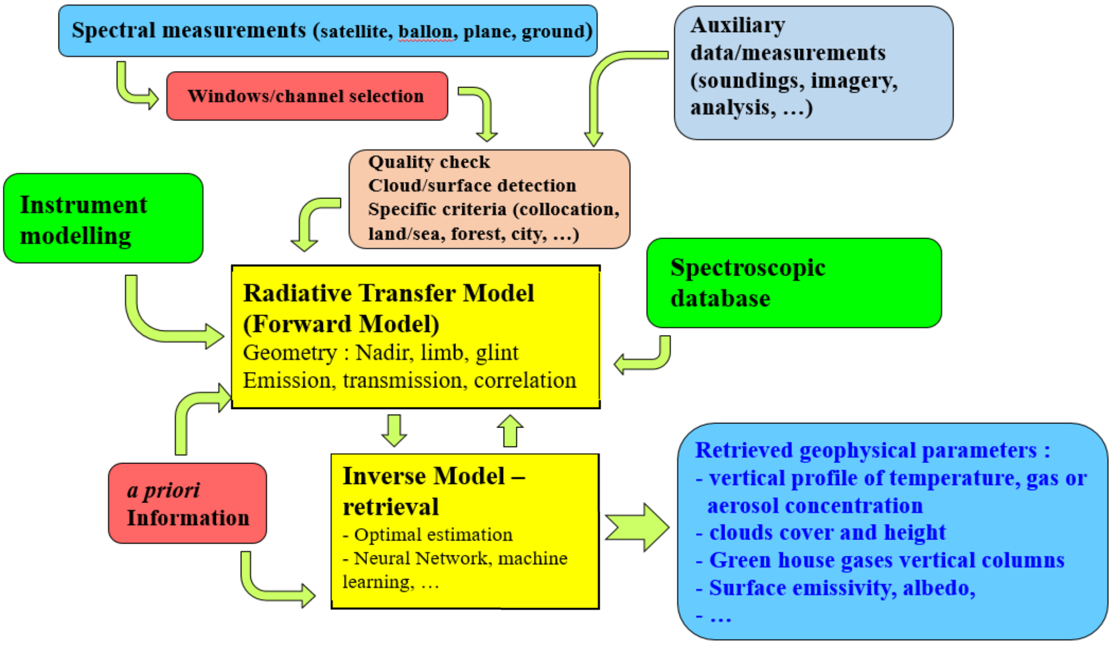

Figure 7. Principal diagram of the retrieval of atmospheric parameters from remote sensing measurements

When the direct problem is solved by an appropriate radiative transfer model, it is necessary to build an accurate and efficient retrieval method (often iterative, often with dumping because "ill posed") able to better account for the information content in the measured atmospheric signal. In addition, it is necessary for operational processing purposes, to automate processes and to optimize the calculation time. Sometimes approximations have to be applied and finally the ultimate accuracy that could be reached with a more meticulous algorithm might not be obtained. A complete description of the main commonly-used methods is given by (Rodgers 2000). The method called "optimal estimation" is a regularized matrix inverse method based on Bayes' theorem. Instead of simply minimizing the deviation between data and model by comparing the observations to a set (lookup tables) of individually synthetic spectra (calculated with a radiative transfer model), the optimal estimation model (OEM) instead solves the inverse problem using an iterative scheme. The retrieval problem is generally ill-posed (i.e. observations only are not sufficient to determine perfectly all the parameters of the model) and ill-conditioned (i.e. small changes in the measurements can potentially have a disproportionately large effect on the solution) so there is no single unique mathematical solution. Instead, physically realistic solutions and a range of uncertainty must be defined for the family of possibilities. Following (Rodgers 2000), it is possible to derive the optimal atmospheric state via the inclusion of additional a priori constraints, in the form of an a priori state vector, with an error covariance matrix. Thus successive iterations are used to minimize a cost function that should be a linearization form of the chi-square function (Press et al, 1992).

Today, due to improved performances of instrumentation, we observe a continuous increase of the spectral measurements fluxes, making more and more difficult real time retrieval of geophysical parameters with classical methods. However, there are other methods to "inverse" the atmospheric spectral measurements. One of them is based on artificial neural networks [e.g. (Hadji-Lazaro et al., 1999)]. It is a computational model whose design is inspired schematically from the operation of biological neurons. Neural networks are generally optimized by probabilistic learning methods, especially Bayesian. The field of atmospheric retrieval is now open to deep learning and artificial intelligence (see (Lary et al., 2016), for instance).

6. Ground-based FTIR measurements technique for the monitoring of atmospheric pollutants and greenhouse gases

Ground-based Fourier transform infrared (FTIR) spectroscopy is widely used, c.f. international networks NDACC-IRWG (NDACC) and TCCON (TCCON), to monitor atmospheric trace gases (pollutants, greenhouse gases, …). In a growing world of more than 7 billion inhabitants, emissions of anthropogenic pollutants and greenhouse gases are increasing continuously. Monitoring and control of these atmospheric pollutants and GHG have become a major challenge for public health authorities and for atmospheric scientists, in order to improve our understanding and modelling of air pollution and climate change processes. The very high spectral resolution Fourier transform Spectrometer (FTS-Paris) is a Michelson interferometer from Bruker Optics (Bruker), model IFS-125HR. The instrument FTS-Paris is located in downtown Paris on Jussieu campus of Sorbonne Université (48°50'N, 2°21'E, 60 m a.s.l). Figure 8, extracted from (Té et al., 2010) shows the principle diagram of the ground-based FTIR measurement technique of the FTS-Paris instrument with its sun-tracker. For this solar absorption configuration, the sun-tracker which is installed on the terrace, collects the solar radiation and transfers this latter into the Fourier transform spectrometer. For more details, see (Té et al., 2010). Recently, a new CCD camera system, called CamTracker, is associated in order to lock the sun-tracker direction towards the sun center.

Depending on the atmospheric species to monitor, appropriate optical filter allows to optimize the signal to noise ratio in the infrared spectral range (from 1 to 15 μm). The atmospheric spectra (solar radiation after crossing the atmosphere) contain many rovibrational signatures of the atmospheric constituents. Figure 9 gives an example of few atmospheric species observed by FTS-Paris: CO_2, O_3, CO, CH_4, N_2O, NO_2, CCl_2F_2, OCS, HCl, H_2O,… (Té et al., 2012).

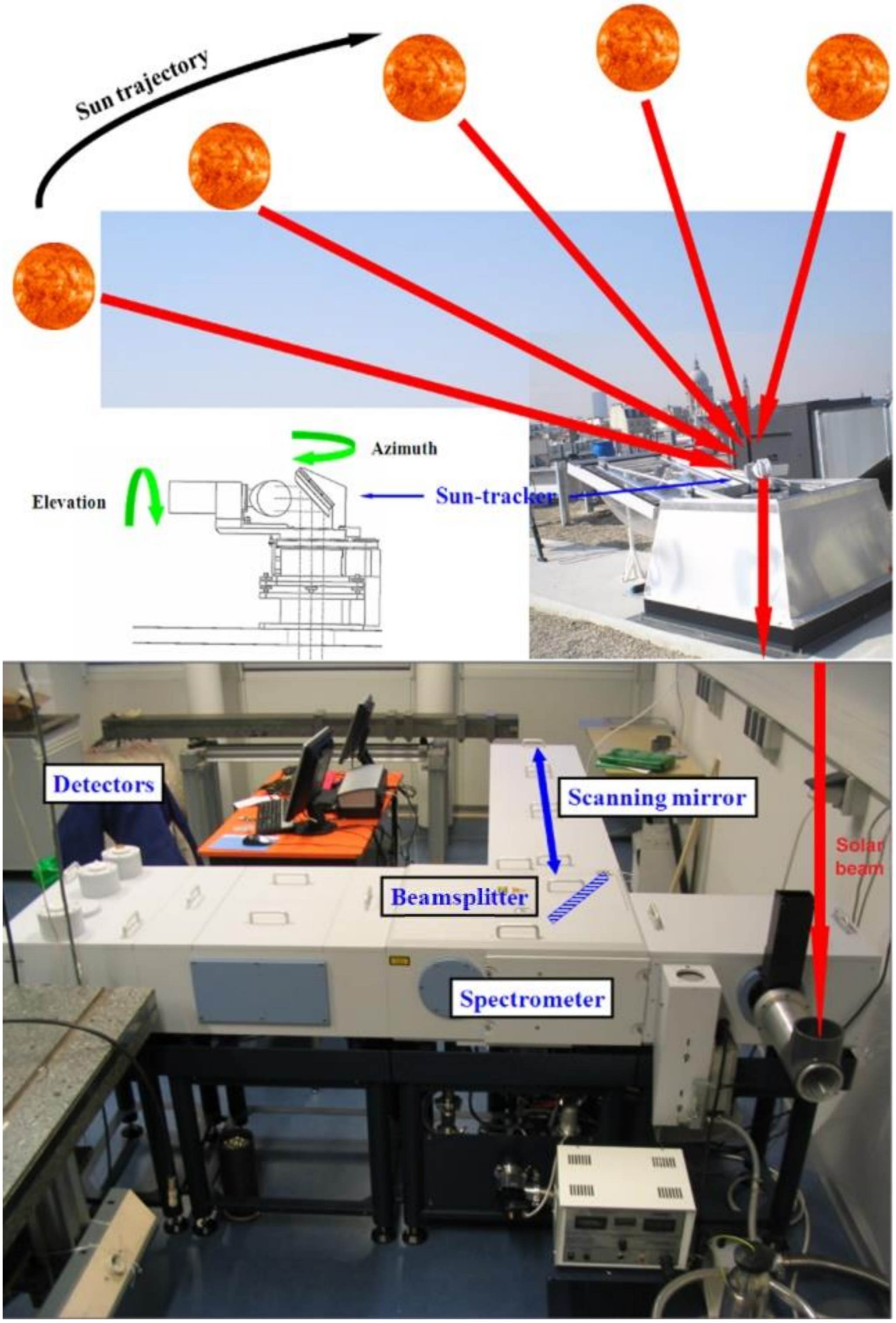

Figure 8. Principle diagram of the FTS-Paris instrument with its sun-tracker

These absorption lines recorded by ground-based FTIR instrument can be used to retrieve their concentration in the atmosphere by processing the experimental spectra with appropriate radiative transfer and inversion algorithms. Several radiative transfer codes exist. For ground-based FTIR measurement, there are for example, SFIT4 (SFIT), GFIT (Wunch et al., 2015), PROFFIT9 (Hase et al., 2004),… The radiative transfer model is based on the Beer-Lambert law:

$$I_{\tilde{v}}(s) = I_{\tilde{v}}(0)T_{\tilde{v}}(0,s) \qquad (1)$$

where $I_{\tilde{v}}(0)$ is the incident solar intensity at the top of the atmosphere, $I_{\tilde{v}}(s)$ is the intensity at the position s along the absorption path and $T_{\tilde{v}}(0,s)$ is the atmospheric transmission between the positions *0* and *s*, which is given by the following equation:

$$T_{\tilde{v}}(0,s) = \exp\left\{-\int_0^s \sum_i^{species} \sum_j^{lines} S_{\tilde{v}}(\tilde{v}_j, i, T(s'))\Phi_{\tilde{v}}(\tilde{v}_j, i, T(s'), p(s')N_i(s')ds')\right\} \qquad (2)$$

where $S_{\tilde{v}}$ is the intensity of line j at spectral position $\tilde{v}_j$ of the species i. $T(s')$ is the temperature in the atmosphere at the position s' along the atmospheric path. $\Phi_{\tilde{v}}$ is the normalised line profile which is typically a Voigt function depending on $\tilde{v}_j$, $T(s')$ and $p(s')$ which is the pressure in the atmosphere. $N_i(s')$ is the concentration of the species *i* at position *s'*. The forward model uses several types of parameters (spectroscopic parameters, meteorological data, *a priori* profiles, geometry of the line of sight, …) in order to calculate the theoretical spectrum which is convoluted with the Instrumental Line Shape and then compared to the measured spectrum. Then the inversion model will minimize this difference by modifying the concentration of the species of interest *i*. For more details, see (Té et al., 2012).

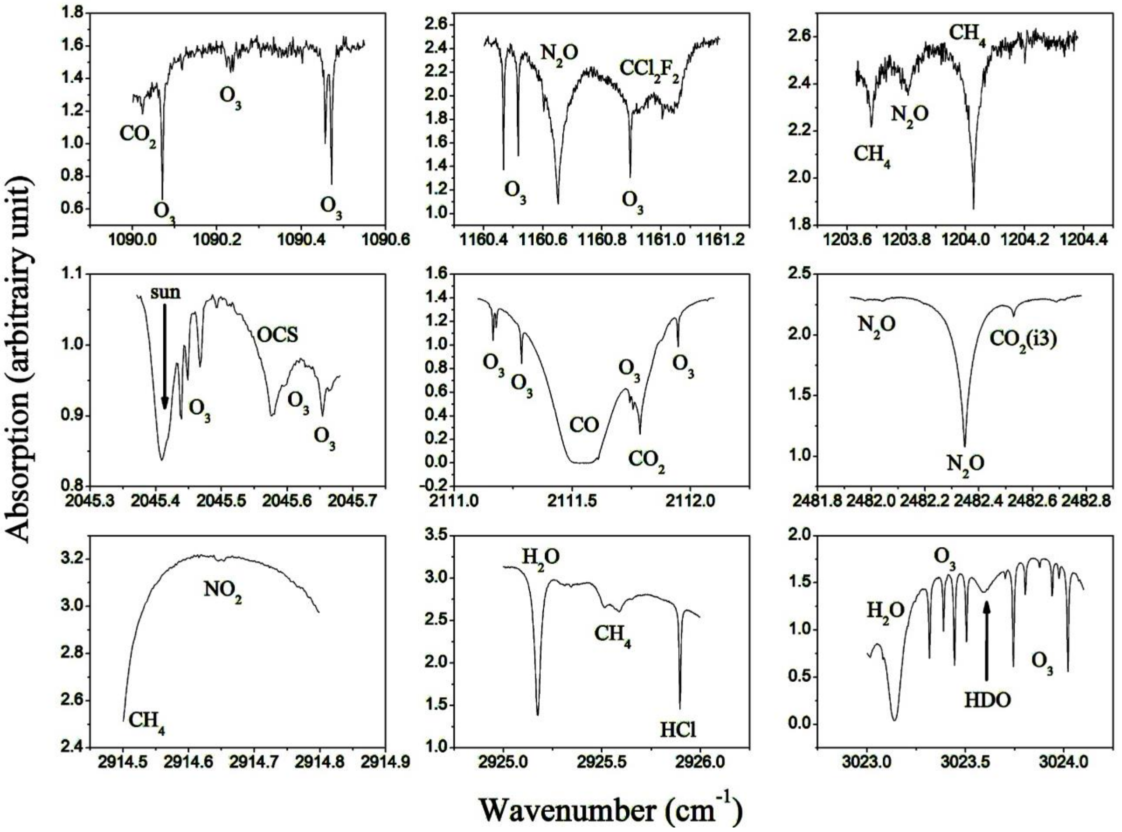

Figure 9. Some of the atmospheric species observed by the FTS-Paris instrument during solar absorption measurement

The FTS-Paris instrument has joined the international network TCCON since September 2014 and records atmospheric data in the near IR spectral domain (1-2.5 µm). We use the GFIT code to analyze all TCCON data which are accessible at https://data.caltech.edu/records/284. The TCCON data are usually used as reference to validate atmospheric models and/or satellite instruments like TANSO-FTS (GOSAT), OCO-2 (LeoStar-2) see (Wunch et al., 2017), TROPOMI (Sentinal-5P), … In parallel, the instrument records also spectra in the middle IR spectral range (2-15 µm). For these latter data, we use the radiative transfer code PROFFIT9 developed by Frank Hase. The following results were obtained by the PROFFIT9 code. Figure 10 shows the seasonality of the atmospheric carbon monoxide (CO). This first example demonstrates the capabilities of such instrumentation to retrieve partial and/or column. At the top panel, the free tropospheric partial columns of CO were calculated between 2 and 12 km height and monthly averaged over the period from 2009 to 2013, obtained by FTS-Paris (purple stars), the spatial IASI-MetOp instrument (orange squares) and the GEOS-Chem model (black circles). The seasonal variability provides a maximum around March-April and a minimum around September-October (orange sinus function fit). The bottom panel presents the monthly averaged surface CO Volume Mixing Ratio (VMR) over the same time period, obtained by the *in situ* measurement CO11M analyzer (dark green circles) and by FTS-Paris (magenta stars). The seasonality at the surface is shifted about two months as compared to the seasonality of the free troposphere columns. For more details, see (Té et al., 2016). The atmospheric spectra can also be used to study spectrally the spectroscopic parameters consistency (line intensity, broadening coefficient, …). Figure 11 introduces the total columns of ozone (O_3) retrieved from the 5 µm spectral range with respect to the retrieval from the 10 µm region. This second example is given to illustrate the potential of such instrument to evaluate spectroscopic parameters. At the left panel, the results were obtained using the HITRAN 2012 spectroscopic parameters database (H12), the middle panel for GEISA2011 (G11) and the right one for S&MPO 2015 (S15). Each database provides total columns obtained at 5 µm in agreement within ±2% with the results from 10 µm. But when using H12, one of the four spectral windows in the 5 µm region gives total columns which differ from the results obtained by the three other windows. For G11, all four windows are consistent and differ about -2% with respect to the results from 10 µm. Only S15 yields very consistent results, ±1% between 5 and 10 µm. For more details, see (Janssen et al., 2016).

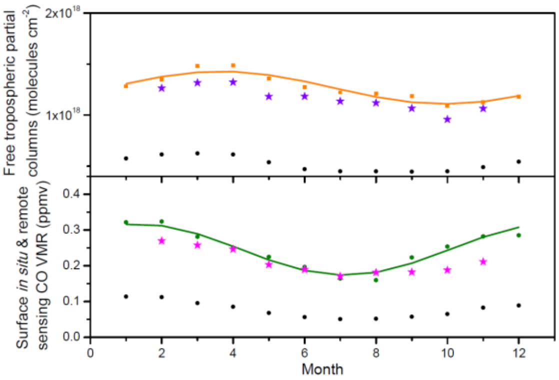

Figure 10. Free tropospheric (top) and surface (bottom) CO at Paris as monthly averages over 5 years

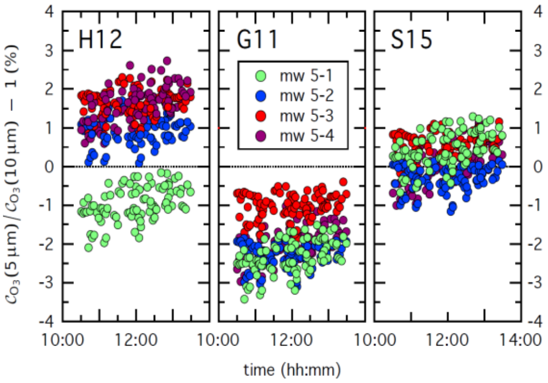

Figure 11. Total ozone column from the 5 µm as relative deviation with respect to the retrieval from the 10 µm. Panels from left to right show results for the H12, G11 and S15 database respectively

7. Examples of atmospheric remote sensing missions using spectroscopic techniques

The continuous increase of atmospheric greenhouse gases over the last decades, generated by anthropogenic activities, is recognized as the main cause for recent climate change with potential damaging impacts. Still, the mechanisms driving the GHGs exchanges between the atmosphere and the Earth surface are poorly understood and this limits our capacity to anticipate the future evolution of GHGs concentrations. Flux measurement is complex to implement and a more common way to monitor GHGs fluxes rely on GHGs concentration measurements and the use of atmospheric transport models. Thanks to the use of atmospheric transport models and sophisticated algorithms, one can retrieve the fluxes from concentration maps but high spatial and temporal resolution is needed to infer GHGs fluxes.

Ground-based instruments give very accurate measurements of concentrations, but they are unequally distributed over the Earth surface. Spatial sampling may be obtained by airborne, shipborne or balloons instruments on a limited area but thanks to the propagation of the electromagnetic waves, it is also possible to implement global atmospheric remote sensing from a very far distance. Spaceborne platforms such as artificial satellites offer a unique viewpoint on the atmosphere that allows global Earth observation from low earth polar orbits (LEO) or frequent measurements of a same area on Earth from geostationary orbits (GEO) (see Fig. 12).

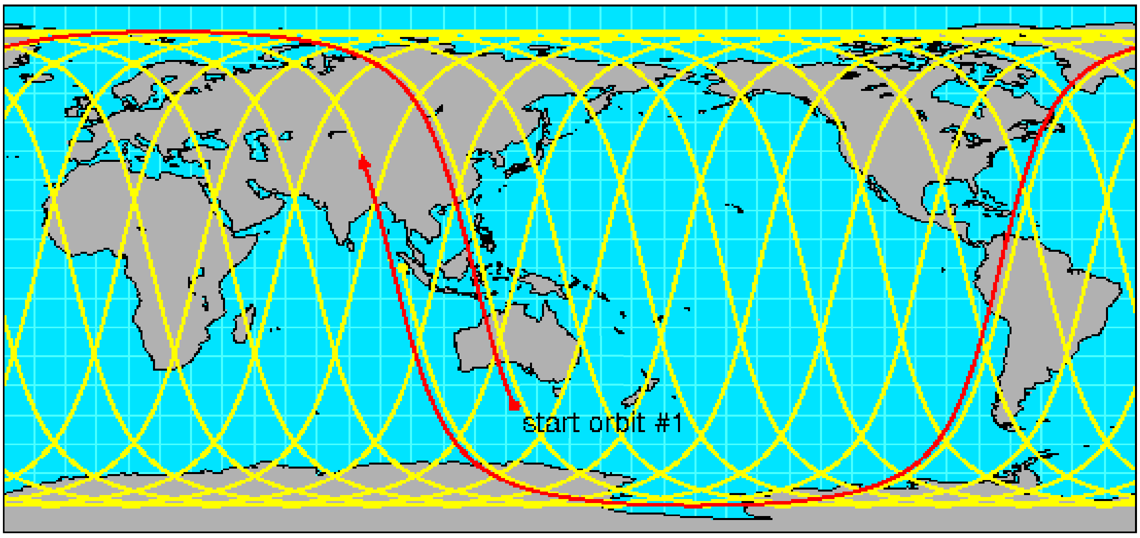

Figure 12. Typical ground paths of the multiple orbital revolutions during one day for a near-polar orbiting satellite

On a general point of view, one can distinguish two categories of space-based atmospheric remote sensing instruments. Passive instruments such as spectrometers observe the Top of Atmosphere radiation, that is the combined result of the different contributions of Sun, Earth and atmosphere radiations transmitted or scattered by the atmosphere. Active instruments such as lidars will use a laser to transmit a light pulse and a receiver with sensitive detectors to measure the backscattered or reflected light by the Earth and its atmosphere.

In the framework of the Vietnam School of Earth Observation, we have introduced two greenhouse gases remote sensing space missions being currently developed at CNES. The first one being the Microcarb mission (MicroCarb) (French-UK mission, target launch date : 2021) that will carry a spectrometer, thus a passive instrument, devoted to the measurement of CO_2 atmospheric mixing ratio and the second one being the MERLIN mission (Ehret et al., 2017) (French-German mission, target launch date: 2022) that will carry a lidar, thus an active instrument, devoted to the measurement of CH_4 concentrations.

Both Microcarb and Merlin measurement principles rely on the theory of molecular spectroscopy as the estimation of the greenhouse gases atmospheric concentrations will be derived from the top of atmosphere radiation measurements at different wavelengths corresponding to different GHG absorption strengths.

MERLIN, for instance, will measure the light scattered and reflected from the Earth's surface and atmosphere which will be illuminated by laser pulses at two slightly different wavelengths, called λ_{on} and λ_{off}. λ_{on} corresponds to an absorption line of CH_4, and the measurement at λ_{off} serves as a reference measurement with negligible radiation absorption by CH_4 (see Fig. 13).

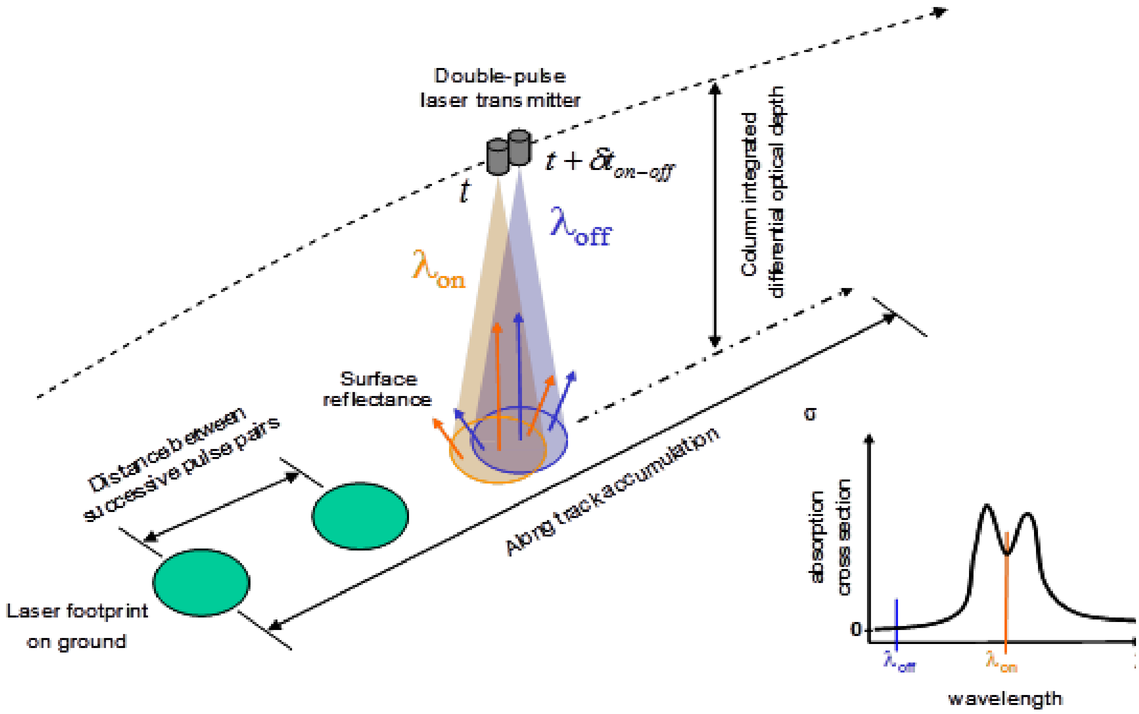

Figure 13. Measurement principle of Merlin CH4 Lidar instrument

Microcarb instrument is a passive spectrometer that will analyze the sun irradiance reflected by the Earth in four spectral bands in the short wave infrared (SWIR) domain at very high spectral resolution. While the sunlight crosses the atmosphere twice, it is partially absorbed by the different atmospheric species. Absorption lines in the solar spectrum appear at wavelengths related to the encountered molecules. The depths of these lines are directly related to the quantity of absorbent molecules. Sophisticated algorithms based on molecular spectroscopy and radiative transfer theories (see the above sections) will be used to retrieve CO_2 atmospheric concentrations (see Fig. 14).

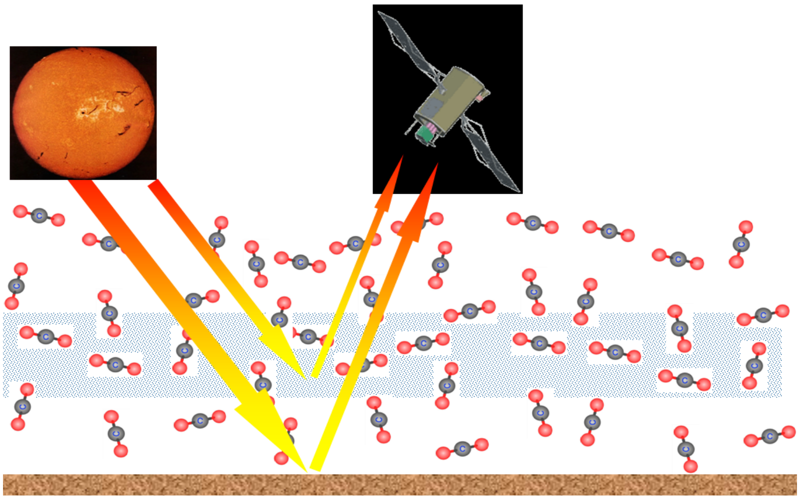

Figure 14. Measurement principle of Microcarb CO_2 spectrometer

For both Merlin and Microcarb missions, one easily understands that the greenhouse gases measurement performances will result from instrument design but will also strongly depend on observation conditions (altitude, sun illumination, satellite speed along the orbit,…). That's why a global view of the issues related to the design drivers of an atmospheric space mission was presented during this first VSEO.

Furthermore, the comparison of the different design choices for two greenhouse gases remote sensing missions was used as a pedagogical tool to allow the students to comprehend the impact of the different design drivers (orbit parameters, satellite pointing modes, instrument design) on the mission products and results.

8. Conclusion and perspectives

Molecular spectroscopy is a powerful tool for remote sensing of the Earth atmosphere. In order to better understand the different atmospheric processes, new atmospheric remote sensing experiments with challenging precision requirements are needed. In this context, laboratory studies are essential to provide accurate data and to develop new and highly sensitive observation techniques. Huge theoretical and experimental efforts need to be made in order to improve our knowledge on molecular spectroscopy as well as improve the accuracy of spectroscopic data for atmospheric remote sensing applications.

Acknowledgements

The authors would like to thank "Rencontres du Vietnam", the University of Science and Technology of Hanoi and Centre National d'Études Spatiales for valuable supports for the organization of the first edition of the Vietnam School of Earth Observation. Thanks are due to Sorbonne Université and Région Île-de-France for their financial contributions as well as to Institut Pierre-Simon Laplace for support and facilities.

References

Berman P.R., 1972. Speed-dependent collisional width and shift parameters in spectral profiles. Journal of Quantitative Spectroscopy & Radiative Transfer, 12, 1331.

Bray C., Cuisset A., Hindle F., Bocquet R., Mouret G., Drouin B.J., 2017b. CH_3D photomixing spectroscopy up to 2.5 THz: New set of rotational and dipole parameters, first THz self-broadening measurements. Journal of Quantitative Spectroscopy & Radiative Transfer, 189, 198–205.

Bray C., Cuisset A., Hindle F., Mouret G., Bocquet R., Boudon V., 2017. Spectral lines of methane measured up to 2.6 THz at sub-MHz accuracy with a CW-THz photomixing spectrometer: Line positions of rotational transitions induced by centrifugal distortion. Journal of Quantitative Spectroscopy & Radiative Transfer, 203, 349–354.

Bruker, https://www.bruker.com/products/infrared-near-infrared-and-raman-spectroscopy/ft-ir-research-spectrometers/ifs-125hr/overview.html.

Clerbaux C., et al., 2009. Monitoring of atmospheric composition using the thermal infrared IASI/MetOp sounder. Atmospheric Chemistry and Physics, 9, 6041–6054.

Dicke R.H., 1953. The effect of collision upon the Doppler width of spectral lines. Phys Rev, 89, 472.

Ehret G., Bousquet P., Pierangelo C., Alpers M., Millet B., Abshire J., Bovensmann H., Burrows J., Chevallier F., Ciais P., Crevoisier C., Fix A., Flamant P., Frankenberg C., Gibert F., Heim B., Heimann M., Houweling S., Hubberten H., Jöckel P., Law K., Löw A., Marshall J., Augusti-Panareda A., Payan S., Prigent C., Rairoux P., Sachs T., Scholze M., Wirth M., 2017. MERLIN: A French-German space lidar mission dedicated to atmospheric methane, Remote Sensing, 9(10), 1052. Doi:10.3390/rs9101052. from spectra in the 1.6 and 2.1 μm regions. Atmos Chem Phys, 9, 7303–7312.

Goody R.M., Yung Y.L., 1996. Atmospheric Radiation: Theoretical Basis. Oxford University Press (Second Edition), ISBN 978-0-19-510291-8, 534p.

Gordon I.E., et al., 2017. The HITRAN2016 molecular spectroscopic database. Journal of Quantitative Spectroscopy & Radiative Transfer, 203, 3–69.

GOSAT (Greenhouse gases Observing SATellite)/ Ibuki. https://directory.eoportal.org/web/eoportal/satellite-missions/g/gosat, and references therein.

Grau E., Gastellu-Etchegorry J.-P., 2013. Radiative transfer modeling in the Earth-Atmosphere system with DART model, Remote Sensing of Environment, 139, 149–170.

Hadji-Lazaro J., Clerbaux C., Thiria S., 1999. An inversion algorithm using neural networks to retrieve atmospheric CO total columns from high-resolution nadir radiances, J. Geophys. Res., 104 (D19), 23841–23854.

Hartmann J.-M., Boulet C., Robert D., 2008. Collisional effects on molecular spectra: Experiments and models, consequences for applications. Elsevier, Amsterdam.

Hartmann J.-M., Tran H., Armante R., Boulet C., Campargue A., Forget F., Gianfrani L., Gordon I., Guerlet S., Gustafsson M., Hodges J. T., Kassi S., Lisak D., Thibault F., Toon G. C., 2018. Recent advances in collisional effects on spectra of molecular gases and their practical consequences. Journal of Quantitative Spectroscopy & Radiative Transfer, 213, 178–227.

Hartmann J.-M., Tran H., Toon G.C., 2009. Influence of line mixing on the retrievals of atmospheric CO_2 Hase F., Hannigan J. W., Coey M. T., Goldman A., Höpfner M., Jones N. B., Rinsland C. P., Wood S. W., 2004. Intercomparison of retrieval codes used for the analysis of high-resolution: ground-based FTIR measurements. Journal of Quantitative Spectroscopy & Radiative Transf, 87, 25–52.

Hindle F., Bray C., Hickson K., Fontanari D., Mouelhi M., Cuisset A., Mouret G., Bocquet R., 2017. Chirped Pulse Spectrometer Operating at 200 GHz. J. Infrared Milli Terahz Waves, 39, 105–119.

Janssen C., Boursier C., Jeseck P., Té Y., 2016. Line parameter study of ozone at 5 and 10 μm using atmospheric FTIR spectra from the ground: A spectroscopic database and wavelength region comparison. Journal of Molecular Spectroscopy, 326, 48–59.

Lary D.J., Alavi A.H., Gandomi A.H., Walker A.L., 2016. Machine learning in geosciences and remote sensing. Geoscience Frontiers, 7(1), 3–10.

Le T., Fissiaux L., Lepère M., Tran H., 2016. Isolated line shape of methane with various collision partners. J Quant Spectrosc Rad Transf, 185, 27–36.

Liou K.-N., 2002. An introduction to atmospheric radiation, Amsterdam; Boston: Academic Press. International geophysics series, ISBN 0-12-451451-0, 84, 583p.

Martin-Drumel M.A., Eliet S., Pirali O., Guinet M., Hindle F., Mouret G., Cuisset A., 2012. New investigation on THz spectra of OH and SH radicals (X-2 Pi(i)). Chem. Phys. Lett., 550, 8–14.

Martin-Drumel M.A., Roucou A., Brown G.G., Thorwirth S., Pirali O., Mouret G., Hindle F., McCarthy M.C., Cuisset A., 2016. High-resolution spectroscopy of six $SOCl_2$ isotopologues from the microwave to the far-infrared. Journal of Chemical Physics, 144, 084305.

MicroCarb (Carbon Dioxide Monitoring Mission). https://directory.eoportal.org/web/eoportal/satellite-missions/m/microcarb, and references therein.

Miller C.E., Brown L.R., Toth R.A., Benner D.C., Devi V.M., 2005. Spectroscopic challenges for high accuracy retrievals of atmospheric CO_2 and the Orbiting Carbon Observatory (OCO) experiment. C R Phys., 6, 876–887.

Miller C.E., et al., 2007. Precision requirements for space-based data. J Geophys Res 112, Doi: 10.1029/2006JD007659.

Mouret G., Guinet M., Cuisset A., Croizé L., Eliet S., Bocquet R., Hindle F., 2013. Versatile Sub-THz Spectrometer for Trace Gas Analysis, I.E.E.E. Sensors, 13, 133–138.

NDACC, Network for the Detection of Atmospheric Composition Change - Infrared Working Group. https://www2.acom.ucar.edu/irwg.

Ngo N.H., Lisak D., Tran H., Hartmann J.-M., 2013. An isolated line-shape model to go beyond the Voigt profile in spectroscopic databases and radiative transfer codes. J Quant Spectrosc Rad Transf. 129, 89–100.

OCO-2 (Orbiting Carbon Observatory-2). https://directory.eoportal.org/web/eoportal/satellite-missions/o/oco-2, and references therein.

Press W.H., Teukolsky S.A., Vetterling W.T., Flannery B.P., 1992. Numerical Recipies in fortran (second edition), Cambridge University Press, Cambridge.

Rodgers C.D., 2000. Inverse methods for atmospheric sounding: theory and practice, World Scientific, Singapore.

Roucou A., Dhont G., Cuisset A., Martin-Drumel M.A., Thorwirth S., Fontanari D., Meerts L. W., 2017. High-resolution study of the rovibrational fundamental bands of thionyl chloride: Interplay of an evolutionary algorithm and a line-by-line analysis. J. Chem. Phys., 147, 054303.

Roucou A., Fontanari D., Dhont G., Jabri A., Bray C., Hindle F., Mouret G., Bocquet R., Cuisset A., 2018. Full Conformational Landscape of 3-Methoxyphenol Revealed by Room Temperature mm-wave Rotational Spectroscopy Supported by Quantum Chemical Calculations. Chem. Phys. Chem, 19, 1–8.

SFIT,https://wiki.ucar.edu/display/sfit4/Infrared+Working+Group+Retrieval+Code%2C+SFIT

Stamnes K., Thomas G.E., Stamnes J.J., 2017. Radiative Transfer in the Atmosphere and Ocean by Knut Stamnes. Cambridge Core.

TCCON, Total Carbon Column Observing Network. https://tccon-wiki.caltech.edu/.

Té Y., Dieudonné E., Jeseck P., Hase F., Hadji-Lazaro J., Clerbaux C., Ravetta F., Payan S., Pépin I., Hurtmans D., Pelon J., Camy-Peyret C., 2012. Carbon monoxide urban emission monitoring: a ground-based FTIR case study. J. Atmos. Oceanic Technol., 29, 911–921.

Té Y., Jeseck P., Franco B., Mahieu E., Jones N.B., Paton-Walsh C., Griffith D.W.T., Buchholz R.R., Hadji-Lazaro J., Hurtmans D., Janssen C., 2016. Seasonal variability of surface and column carbon monoxide over megacity Paris, high altitude Jungfraujoch and Southern Hemispheric Wollongong stations. Atmos. Chem. Phys., 16, 10911–10925.

Té Y., Jeseck P., Payan S., Pépin I., Camy-Peyret C., 2010. The Fourier transform spectrometer of the UPMC University QualAir platform. Rev. Sci. Instrum., 81, 103102.

Tennyson J., Bernath P.F., Campargue A., Csaszar A. G., Daumont L., Gamache R.R., Hodges J.T., Lisak D., Naumenko O.V., Rothman L.S., Tran H., Zobov N.F., Buldyreva J., Boone D.C., Hartmann J.-M., McPheat R., Weidmann D., Murray J., Ngo N.H., Polyansky O.L., 2014. Recommended isolated-line profile for representing high-resolution spectroscopic transitions. Pure Appl Chem, 86, 1931–1943.

Wunch D., Toon G.C., Sherlock V., Deutscher N.M., Liu X., Feist D.G., Wennberg P.O., 2015. The total carbon column observing network's ggg2014 data version. Doi: 10.14291/tccon.ggg2014.documentation.R0/1221662. 37, 45, 55, 95, 125.

Wunch D., et al., 2017. Comparisons of the Orbiting Carbon Observatory-2 (OCO-2) XCO_2 measurements with TCCON. Atmos. Meas. Tech., 10, 2209–2238.

Zhakarenko O., Motiyenko R.A., Avilès-Moreno J.R., Jabri A., Kleiner I., Huet T.R., 2016. Torsion-rotation-vibration effects in the ground and first excited states of methacrolein, a major atmospheric oxydation product of isoprene. J. Chem. Phys., 144, 024303.