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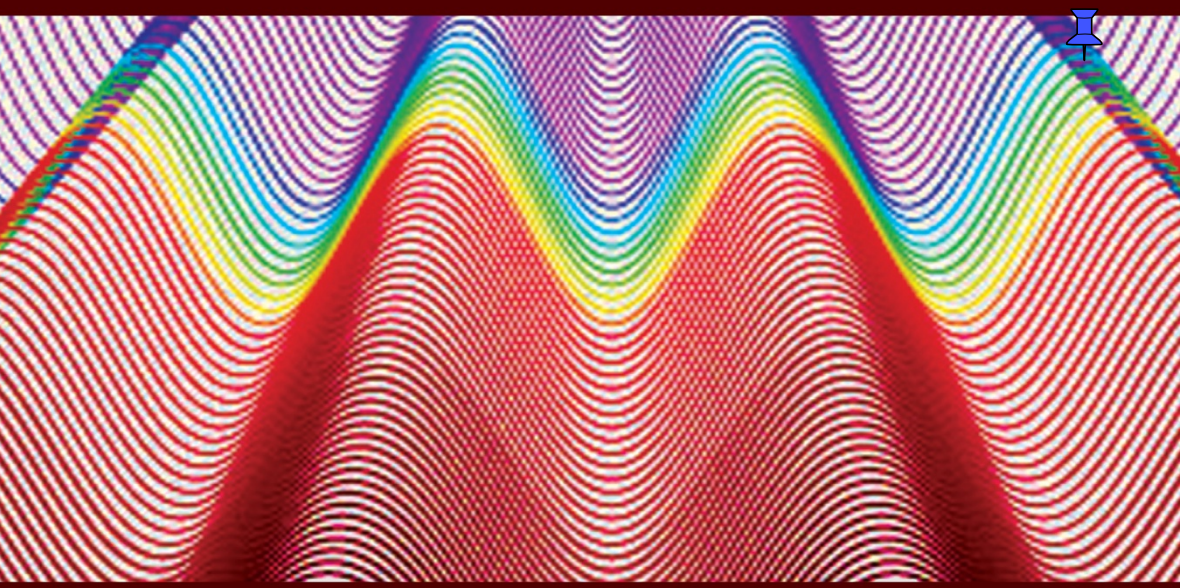
INFRARED SPECTROSCOPY SET



Volume 4

Infrared Spectroscopy of Symmetric and Spherical Top Molecules for Space Observation 2

Pierre-Richard Dahoo
Azzedine Lakhlifi

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coordinated by
Pierre Richard Dahoo and Azzedine Lakhlifi

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Foreword

Spectroscopy is the high road to physico-chemical measurements of astrophysical objects, such as the interstellar medium, stars or planets and exoplanets. In recent decades, the understanding of the increasingly finer details of the interaction between matter and radiation, as reflected in the spectral range by effects, sometimes unexpected, on the observed spectra, has led to outstanding advances in spectroscopy, from ground- or space-based observations. For this purpose, increasingly sophisticated instruments were developed for space probes, initially inspired by laboratory instruments, in order to cope with the severe constraints of space observation and exploration.

The challenge of laboratory spectroscopy presented in this book, the fourth volume in this series, resides not only in registering increasingly complex spectra, even for the simplest molecules observed at high temperature or excited to high vibrational states, but also in understanding specific molecular mechanisms, such as the spectroscopy of molecules in rare gas matrices, clathrates or physico-chemical mechanisms related to the adsorption on graphite substrates. These mechanisms can be used to extrapolate to the very specific conditions of the interstellar medium, where the very rich chemistry discovered by the observations in the millimetric range in the last 50 years is highly dependent on ion–molecule–substrate mechanisms.

Spatial instrumentation in remote spectroscopy offers the possibility of exploring planets with atmospheres, particularly by means of instruments with medium to high resolution. However, Earth observations should be treated separately, as they have other objectives, particularly operational ones, and a different approach and constraints compared to the various distant exploration missions, even though they involve similar categories of instruments. Fourier transform spectrometers have measured, in particular, the atmospheres of Mars, Venus and giant planets and their

satellites, thanks to their performances in combining large spectral extent and (relatively) high resolution. The pioneering missions were Mariner, Venera and Voyager. Grating or prism spectrometers, particularly those using adjustable prisms (AOTF – Acoustic Optic Tunable Filter), have also provided remarkable results on Mars and Venus. After the first observations using variable circular filter spectrophotometry (IKS on Vega probe), comets, with their highly specific atmosphere, were observed with grating spectrometers (VIRTIS on Rosetta), which led to a better understanding of their composition and revealed surprising isotopic ratios.

Substrate spectroscopy issues are connected with planetary studies in order to understand the adsorption chemistry at play in the interstellar medium, as well as in the very high atmosphere of planets: one of the key results of the Cassini mission showed that the complex hydrocarbons observed on Titan were generated not only from the photochemistry of nitrogen or methane atmosphere at the level of high clouds, but also in the ionic chemistry of the very high atmosphere, measured directly using mass spectrometry from the instrument aboard the Cassini during its flight over Titan.

There is no doubt that there is still room for embedded spectroscopy to significantly evolve into future space missions: Raman spectroscopy methods, still fresh on planetary probes (Mars Curiosity and Perseverance missions), LIDAR observations or the CRDS technique will lead the way to new advances, which laboratory techniques and theoretical models will help to interpret. The joint progress of various disciplines of chemistry, spectroscopy and of Earth and universe sciences is a remarkable example of a coordinated multidisciplinary approach that involves the joint research efforts of laboratories of various specializations. This book, the fourth volume in the series “Infrared Spectroscopy of Molecules for Space Observation”, focuses on the context and results of this research.

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June 2021

Preface

The observable universe is visible thanks to the light that reaches us from the point being observed. These extreme points form the contour of a sphere, whose limit lies at the cosmological horizon, with the Earth at its center. Other observers, located elsewhere in the universe, see a different observable sphere of the same radius. It is a relative notion. Let us recall that in cosmology, the unit of measurement for distances is the light-year, which is the distance that light travels in one year, which corresponds to about $9.5\ 10^{12}$ km. The megaparsec, which amounts to 3.26 million ($3.26\ 10^{6}$) light-years, is another unit of distance used particularly in extragalactic astrophysics. The Standard Model of Cosmology elaborated at the beginning of this century, by 2000, is perhaps the most successful model presently that offers a description of the evolution of the universe, in terms of the major stages in the history of the observable universe, as well as its current composition resulting from astronomers' observations. In order to explain the myriad of observable galaxies and planetary systems, suns and black holes, cosmologists proposed an inflationary model.

As mentioned in the prefaces of the previous volumes, the universe is a preferred spatial environment for astrophysicists, cosmologists, astronomers and physicists, both for observations and for testing the theory of general relativity of Albert Einstein by means of predicted and observed phenomena, elaboration of new theories and their expected confirmation by observations. This is the context in which the Nobel Prize for Physics was awarded to Sir Roger Penrose in 2020, for his work on the existence of black holes based on the theory of general relativity, and to astronomers Andrea Ghez and Reinhard Genzel, for their research on the phenomena observed at the center of the Milky Way galaxy in the Sagittarius A region, where the existence of a black hole was predicted, and who showed that, indeed, a supermassive black hole was present there.

This book, the fourth volume of this series, offers an overview of several experimental instruments used for the observation and analysis of a physico-chemical system, in order to determine relevant characteristics such as the position, intensity and width of IR absorption lines. Some instruments rely on the principle of light interferences, such as the Fourier transform infrared (FTIR) spectroscopy, or on the operating principle of a resonant laser cavity, such as the cavity ring-down spectroscopy (CRDS), or the frequency comb techniques. The species present in a given atmosphere, such as the tholins on Titan (satellite of Saturn), can be prepared *in situ* in the laboratory and studied by spectroscopic ellipsometry, in order to determine their optical properties. This data can be used to calculate the albedo, for example. A spectrometer employing an acoustic optic tunable filter (AOTF) was used to obtain IR data on Mars and Venus from Mars Express and Venus Express missions. Data analysis made it possible to identify the nature of certain observations in the IR spectrum and to eliminate possible ambiguities. Hence, the absorption by the 628 CO_2 isotopic species could be confirmed at the expense of a possible absorption by a C–H bond in the same IR spectrum. Finally, LIDAR is the preferred instrument for observing distant objects and species present in the atmosphere of planets, in a given environment.

This volume, however, focuses on the applications of the theoretical models described for diatomic and triatomic molecules to symmetric tops such as NH_3 and/or spherical tops such as CH_4, when they are in an environment that may be present in the universe, i.e. when they are trapped in a nanocage of rare gas matrix, clathrate, fullerene or adsorbed on a graphite substrate. All of these models are theoretical instruments for the simulation-based observation of a molecule. The results of these theoretical models should be compared with those of experimental observations, using instruments that are specifically developed for various observation situations. The latter may be related to the observation site, such as a laboratory, an observatory or a space probe, or a telescope in space. They may also relate to the type of molecular system observed, molecules or chemical species (ions, radicals, macromolecules, nanocages, etc.) that compose, on the one hand, the atmospheres of planets, the Earth or the planets of the solar system and possibly their satellites, and on the other hand, the interstellar media, the comets or the exoplanets throughout the spatial extent of the universe, estimated by the cosmologists as 10^{23} km.

As underlined in Volumes 1, 2 and 3, theoretical and experimental approaches to spectroscopies led to the development of methods and instruments for the observation and analysis of the spectral characteristics of chemical species, molecules, radicals and ions in specific environments. Volumes 1 and 2 of this series [DAH 17] describe the theoretical models developed in order to determine the absorption spectra of diatomic molecules (homonuclear or heteronuclear),

triatomic molecules (linear or nonlinear, symmetric or non-symmetric) in the gas phase and particularly when they are trapped in the nanocages of inert matrices of rare gases, or hydrate clathrates at a very low temperature. Volume 3 deals with the spectroscopy of symmetric and spherical tops in the gas phase.

This book (Volume 4) is a continuation of Volume 3, focusing on the application of theoretical models for the simulation of IR spectra of symmetric or spherical top species evolving in various media. The method of an extended substitution model is explained in terms of the determination of the type of symmetry of the environment in the immediate vicinity of the trapped molecule. The objective is to propose theoretical spectra that match with experimental IR data and hence identify molecules based on transitions and profiles, not only in the gas phase, but also when they are constrained to evolve in an environment, such as a nanocage or a surface.

Chapter 1 provides a brief overview of the instruments developed and used in the laboratory for the study or observation of molecules, FTIR spectroscopy or laser cavity spectroscopy. An example of embedded instruments such as SPICAM, SPICAV or SOIR aboard an orbiter or a space probe serves to illustrate the instrumental context of space observation and of the international collaboration required to develop measurement instruments, as well as the analysis methods for the identification according to the scientific norms of the molecules that may be present in the probed atmosphere, such as on Mars or Venus during Mars Express and Venus Express missions. Aerosol characterization by spectroscopic ellipsometry is also discussed as a non-standard method. The LIDAR technique, which is used for observing the terrestrial atmosphere, is also described.

Chapter 2 presents various contributions to the interaction potential energy between the studied molecule and its solid environment, considering the hypothesis of binary interactions: “studied molecule – molecule or atom of the environment”. The quantum “dispersion–repulsion” contribution is modeled by an atom–atom Lennard-Jones potential energy type, while the electrical contribution is modeled by a charge–charge potential energy in the case of clathrate nanocages or multipole–multipole in the case of nanocages of rare gas, fullerene or graphite substrate matrix.

Chapter 3 provides a description of the substitution model applied to the study of NH_3 in rare gas matrices. An atom–atom potential is used to calculate the interaction between the trapped molecule and its environment. A numerical method is applied to determine the perturbed motions of the molecule. The IR spectral profiles are determined and compared to the experimental spectra. The influence of lattice phonon modes on the shift and width of spectral lines is also discussed.

Chapters 4 and 5 provide a description of the extended substitution model, based on the effect of the local symmetry around the equilibrium position of the molecule in the cage for calculating IR spectra in natural nanocages, such as clathrates and fullerene. This model relies on the substitution model used for building theoretical models in IR spectroscopy in rare gas matrices. The model is applied to CH_4 and NH_3 molecules included in clathrate nanocages (Chapter 4) and NH_3 in a fullerene nanocage.

In Chapter 6, the theoretical models developed in Volumes 1 and 2 to deal with the adsorption of diatomic and triatomic molecules on a graphite substrate, are applied to the NH_3 molecule in order to determine the IR absorption spectra at a very low temperature. This substrate is often used to model the surface of interstellar dust grains.

Pierre Richard DAHOO
Azzedine LAKHLIFI
June 2021

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IR Spectra in Space Observation

The IR (infrared) range corresponds to the frequency band between 10^4 GHz and 5×10^5 GHz, therefore to wavelengths ranging between 0.78 μm and 1,000 μm. According to the ISO system (ISO 20473, 2007), this range is divided into three regions corresponding to near IR from 780 nm to 3,000 nm (sunlight), mid-IR from 3 μm to 50 μm (thermal source) and far IR from 50 μm to 1,000 μm (source in astronomy). For a given electronic state, the interaction between an electromagnetic wave in this range and a physical system in gas, liquid, solid or possibly plasma state is reflected by a transition between two vibrational and/or rotational energy states of the system, which are discrete and/or in the continuum. The possible physico-chemical processes, such as the absorption and emission of photons, elastic (Rayleigh) scattering and inelastic (Raman, Compton) scattering, dissociation, ionization and various possible combinations and interferences of these phenomena can be observed using optical instruments, such as spectrometers or telescopes. These instruments can operate on site in a laboratory or from an observatory or in the space (aboard a space probe). Depending on the latter sites and the system under observation, various options should be considered for the successful completion of an observation process.

1.1. Introduction

In a laboratory, experimental IR spectroscopy of atmospheric molecules is mainly studied in the gas phase.

Taking into account the shape of the absorption line (Gaussian by Doppler effect, Lorentzian by pressure-induced broadening) [DAH 88, DAH 97, DAH 16a,

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DAH 17], the intensity of a vibration–rotation absorption line in the gas phase is given by the expression:

$$S_{if}^{g} = \int_{\sigma_{\min}}^{\sigma_{\max}} \frac{8\pi^3}{3hc}\sigma_{if} f(\sigma-\sigma_{if}) N\left[1-\exp\left(-\frac{hc}{k_B T}\sigma_{if}\right)\right] g_i \frac{\exp(-hc\sigma_i / k_B T)}{Q(T)} R_{if}^2 \, d\sigma \quad [1.1]$$

where σ_{if} is the wave number (in cm^{-1}) of the considered rovibrational transition, N is the number of molecules per unit volume, $hc\sigma_i$ is the energy of the initial level, $Q(T)$ is the total partition function of the molecule at temperature T, R_{if} is the moment of rovibrational transition, and finally g_i is the degeneracy due to the nuclear spin of the initial level. The shape of the line is a Voigt function, a convolution product of a Gaussian and a Lorentzian, as the Doppler effect and the broadening by pressure are concomitant, and its integral over the absorption domain is equal to 1 ($1 = \int_{\sigma_{\min}}^{\sigma_{\max}} f(\sigma-\sigma_{if})\, d\sigma$).

In condensed media, when the observed molecule is trapped in a rare gas matrix or in a nanocage of a solid medium, a corrective term reflecting the effect of the refractive index n of the solid medium must be taken into account. If the rotation–vibration interaction is ignored, and the fundamental state is not degenerate ($g_0 = 1$), the intensity of a vibrational line at low temperature, in relation with a molecule is written as:

$$S_{if}^{m} = \int_{\sigma_{\min}}^{\sigma_{\max}} \frac{1}{n}\left(\frac{n^2+1}{3}\right)^2 \frac{8\pi^3}{3hc}\sigma_{if} f(\sigma-\sigma_{if}) \left|R_{if}\right|^2 \, d\sigma \quad [1.2]$$

where R_{if} is the vibrational transition moment. Written in this form, relation 1.2 provides essential information about the dipole transition moments of the vibrational modes in a solid matrix. These quantities can be extracted experimentally from the integrated intensity of the absorption spectrum:

$$S_{if}^{m} = \frac{1}{2lN}\int Ln\frac{I_0(\sigma-\sigma_{if})}{I_t(\sigma-\sigma_{if})} d\sigma = \frac{1}{2lN} I_{if} \quad [1.3]$$

where N is the number of molecules per cm^3, $2l$ is the path length in the sample, and the term under the integral is the integrated absorption measured over the IR absorption spectrum domain. The calculation of physical quantities, such as the lifetime of a level based on the integrated absorption, is explained in chapters 6 and 7 of [DAH 16a] and in the Phd dissertations [ABO 73a, DUB 75, GAU 80, BOI 85] for molecules inserted in a solid rare gas matrix. For dipole moments, the method is

given, for example, in [DAH 88] for CO_2 and N_2O molecules in the gas phase, or [GHE 79] for the CH_4 molecule.

Chapter 3 of Volume 1 of this series provides a description of the method for the measurement and analysis of an absorption line based on the Bouguer–Lambert law, applied to determine the infinitesimal amount of energy absorbed by an elementary thickness of matter. For an intensity $I(\sigma)$ of a radiation of wave number σ traveling through an elementary thickness dl of a gas under pressure P, the resulting variation $dI(\sigma)$ is proportional to $I(\sigma)$ and dl. These hypotheses lead to the following Bouguer–Lambert law:

$$dI(\sigma) = -k(\sigma, P)\, I(\sigma)\, dl \qquad [1.4]$$

where $k(\sigma, P)$ is the absorption coefficient at wave number σ and pressure P. The intensity of the radiation transmitted at wave number σ results from the integration of the previous equation:

$$I_t(\sigma) = I_0(\sigma)\, e^{-k(\sigma,P)l} \qquad [1.5]$$

where $I_0(\sigma)$ is the intensity of the radiation incident on the gas and l is the gas thickness through which the radiation travels.

The actual shape of an absorption line is defined by the following function:

$$A(\sigma) = \frac{I_a(\sigma)}{I_0(\sigma)} = 1 - \frac{I_t(\sigma)}{I_0(\sigma)} \qquad [1.6]$$

which does not take into account the instrumental line shape (infinite resolution hypothesis), with $I_a(\sigma) = I_0(\sigma) - I_t(\sigma)$, where $I_a(\sigma)$ is the intensity of the absorbed radiation.

The previous two equations lead to:

$$A(\sigma) = 1 - e^{-k(\sigma,P)l} \qquad [1.7]$$

Moreover, the profile of the spectral line is defined by the variation of the absorption coefficient $k(\sigma, P)$, which depends on the wave number σ and is given by:

$$k(\sigma, P) = \frac{1}{l} \ln\left(\frac{I_0(\sigma)}{I_t(\sigma)}\right) \qquad [1.8]$$

For a number of active molecules absorbing or emitting weak radiation, leading to the property $k(\sigma, P)\, l \ll 1$, the actual shape of the line coincides with the profile and is expressed as:

$$A(\sigma) \approx k(\sigma, P) l \qquad [1.9]$$

This expression is valid in the real space of the spectrum. In the measurement space, the effect of the instrumental line shape leads to an apparent shape, which is the convolution product of the instrumental line shape and the actual shape. A deconvolution process is required to retrieve the actual spectrum.

The integrated absorption coefficient of the line is defined from its actual profile, by integration over the absorption domain, which is as follows:

$$S = \int_0^\infty k(\sigma, P)\, d\sigma \qquad [1.10]$$

If the active molecules absorb independently of one another (Beer's hypothesis), this coefficient is proportional to the pressure and is written as:

$$S = S^0 P \qquad [1.11]$$

where S^0 is known as the "line intensity".

It is important to note that Beer's hypothesis is not generally verified for each wave number, and as a result, the integrated absorption coefficient is not proportional to the pressure for each wave number. This experimentally determined coefficient is related to the theoretical coefficients expressed by equations [1.1] and [1.2].

The absorption lines corresponding to transitions between energy levels can be determined experimentally, either by frequency-resolved spectroscopy using a spectrometer or an interferometer, or by laser absorption over the absorption spectral range of the line. The recorded spectra are the convolution product of the instrumental line shape and the actual shape of the absorption line. A deconvolution of these spectra is required before the analysis, in terms of the intensity, width and center of the line. The procedure is described in Appendix 1 (section 1.6.1) and relies on the application of the sampling theorem.

Building a setup for experimental observation requires three elements.

The first element is a set containing a light source and a dispersive element for the frequency scanning of the spectral range, if the source is polychromatic. There are classical sources (spectral lamp, black body, etc.) or quantum sources (lasers). The classical light source can be a natural heat source, such as the light from a star or an artificial one, or light emitted by a gas lamp or a heated filament. These are wide spectral band polychromatic sources, whose maximum intensity corresponds to a given wavelength λ_m, which depends on the temperature T according to the law $\lambda_m T$ = constant. For a black body, the constant in Wien's displacement law is equal to 2.897 773 10^{-3} mK. The laser quantum sources are also used in IR spectroscopy in experiments studying system dynamics under radiation, such as laser-induced fluorescence, double resonance (DR), Rayleigh or Raman scattering or the dynamics of radiative or non-radiative relaxation of the populations of energy levels in probe–pump experiments. These are monochromatic or quasi-monochromatic sources of narrow spectral band. A tunable laser can be used to determine the absorption spectrum around a frequency defined by the transition between two energy levels. Resonant cavity spectroscopy, developed as a result of efforts to improve laser sources, involves the insertion of an absorbing molecule in the laser cavity, and then the identification of the absorption due to losses in the laser gain curve.

The second element is the system to be analyzed can be a fluid (gas or liquid), a solid or a plasma medium in a suitable laboratory chamber, or in a natural medium in space. Laboratory settings sometimes use absorption cells filled with fluid (gas or liquid) or a sample holder's surface on which the solid medium is deposited. A multiple-reflection cell is used to increase the absorption path when the transition is weak, in order to reach a convenient signal-to-noise ratio (SNR) for the observation of the absorption line.

Finally, the third element is a data detection and acquisition system that translates the transition induced at each frequency of the incident light on the studied systems into an electrical signal, which after analysis allows the characterization of the system based on its spectral signature.

In formal terms, the experimental setup includes an object space, which is the illuminated system, or an image space, which contains the devices for detection and those of the optical system, which is the set of optical devices in the measurement instrument. IR vibrational and rotational spectroscopy focuses on the processes of photon absorption or emission in a spectral range of low energy molecular spectroscopy. This domain is broader than that corresponding to the IR range, since it spans from microwaves to ultraviolet radiation.

The instruments used in IR spectroscopy essentially rely on electromagnetic wave interferences, in order to separate the spectral components of the radiation

from a classical light source and determine the effect of the observed system on each spectral element used as a probe. These are generally prism spectrographs, grating spectrometers, Michelson interferometers or frequency- and time-resolved laser spectroscopy, since laser development [DEM 96].

This chapter focuses on observation and measuring techniques. The techniques that are essentially used in laboratories for measuring campaigns involve interferential spectroscopy, the use of gratings, laser spectroscopy or polarized light spectroscopy. The chapter ends with an example of the device used on the Mars Express and Venus Express orbiters.

Section 1.2 is dedicated to Fourier transform infrared spectroscopy (FTIR). Given the rich bibliographical references on the subject, only the first works in this field are referenced [JAC 60, BRA 95, CON 66, LOE 66, HUN 68, BEL 72a, CHA 73, GRI 75, GRI 86, DEM 96, JAM 02]. This section includes a description of the operating elements related to technical aspects in the setup for observation or data analysis. Two types of interferometers are described, a laboratory interferometer and a commercial interferometer.

First, a Connes-type Fourier transform interferometer (FTIR) with a very large path difference is described. This apparatus was built at the Molecular Spectronomy Laboratory at the Sorbonne University in Paris, Pierre and Marie Curie campus (formerly Pierre and Marie Curie University). This instrument was operational for the study of gas phase molecules in the atmosphere until the beginning of the 21st century, under the leadership of L. Henry, according to a concept proposed by P. Connes and developed by Valentin and Michel. A model of this type of interferometer is still operational in the Molecular and Atmospheric Spectrometry Group at Reims University. It is important to note that P. Connes, who worked at the Aimé-Cotton Laboratory at Paris Saclay University (formerly Paris South University, of Orsay) and the Director of LAC of that time, Jacquinot have made significant contributions to the development of Fourier transform spectroscopy [CON 92, CON 95].

A commercial type (Brucker IFS 113v) FTIR used in research work on the spectroscopy of molecular species isolated in an inert matrix is also described. The experimental device was used to study a certain number of atmospheric molecules using the isolated matrix technique, by the group led by L. Abouaf-Marguin and L. Schriver-Mazuoli at the Laboratory of Molecular Physics and Applications of Sorbonne University in Paris (formerly Pierre and Marie Curie University in Paris) at the beginning of the 1990s [BRO 93a, ABD 93, LUG 94, DES 94, JAS 95, RAD 95, DAH 97, BAH 97, HAL 98, CHA 00a, CHA 01, COA 03].

The spectroscopy of laser absorption in a resonant cavity is another example of spectroscopy that differs from the classical frequency-resolved and dispersion spectroscopy, using prisms or interference with echelette grating. Further examples are the resonant cavity laser absorption spectroscopy of the intracavity laser absorption spectroscopy (ICLAS) type, or the cavity ring-down spectroscopy (CRDS). These techniques can be used to measure weak absorptions. In France, these techniques were mainly developed by the Interdisciplinary Laboratory of Physics at Joseph Fourier University of Grenoble (LIPhy, former Spectrometry Laboratory) [STO 52, CHE 83, CAM 86, CAM 90, CAM 91, ROM 93, ROM 97a]. It is worthwhile to highlight the pioneering work of the LIPhy researchers in the development of cutting-edge laser techniques and instruments for molecular absorption spectroscopy, such as the continuous wave cavity in ring-down spectroscopy (CW-CRDS) [MOR 05], optical-feedback cavity-enhanced absorption spectroscopy (OFCEAS) [ROM 97a] and mode-locked cavity-enhanced absorption spectroscopy (ML-CEAS) [GHE 02], which were invented or developed for the first time at LIPhy, or the use of a quantum cascade diode [GOR 13] or frequency combs to improve the limits of detection [MON 15]. One section focuses on frequency comb spectroscopy (FCS), which is increasingly used to study molecules [HÄN 06, HAL 06, CUN 01, FOR 19, DID 20].

Section 1.4 provides examples of techniques that were applied for the study of molecules in the atmospheres of planets other than the Earth. It includes a brief description of the spectroscopic ellipsometry technique [AZZ 77], which is used for the study of materials deposited as thin layers on substrates. This technique was used to determine the optical indices of aerosols present in the atmospheres of planets or satellites such as Titan (“tholins”) [SCI 10, CAR 12, MAH 11, SCI 12, MAH 12a, MAH 12b, MAH 12c, MAH 14]. The final part of the section briefly describes the SOIR device used on the Venus Express for the study of the atmosphere of Venus. For the observations conducted from a space probe, an example is the observation device referred to as SPICAM (“Spectroscopy for Investigation of Characteristics of the Atmosphere of Mars”) or SPICAV/SOIR (Solar Occultation in the Infra-Red) aboard the orbiters (Mars Express/Venus Express) and developed (formerly Aeronomy Service SA and former Center for Earth and Planetary studies) in collaboration with Belgian and Russian partners, under the main coordination of Bertaux [NEV 06, BER 07, MAH 08, VIL 08a].

1.2. Fourier transform spectroscopy

Since the development of the first interferometer by Michelson at the end of the 19th century [MIC 81, MIC 82], interferometric spectroscopy or Fourier transform spectroscopy using interferometers has gradually replaced classical spectroscopy, by grating spectrometers for the measurement and analysis of absorption spectra in the

IR range. The technique of interferometric spectroscopy, later referred to as Fourier transform spectroscopy, was proposed by Jacquinot [JAC 60, CON 92] in the 1960s. The state-of-the-art for the optical field in France in the 1960s can be found in [AMA 62]. Jacquinot [JAC 60] describes the methods for selecting wavelengths by the frequency of interferometric modulation. The spectrum is not directly recorded in its common form, but in the form of an interferogram that is the Fourier transform of the spectrum. Similar to the photographic methods, the main advantage of this method is that the time required for recording the interferogram does not depend on the width of the spectral range. The resolution and the luminosity of the measuring process are considered, as well as the various methods for spectrum reconstruction from the interferogram.

The evolution of grating spectrometers or spectrographs towards interferometers was made possible by the works of the following scientists:

– Fellgett [FEL 49, FEL 58] on the advantages of the "multiplex" method or Fellgett's advantage; at each time t, an FTIR spectrometer simultaneously records the spectral data at all of the wavelengths at high resolution, over an extended spectral range. A grating spectrometer or a spectrograph measures the intensity of an absorption or emission line over a very narrow spectral range around a given wavelength, during the measurement of a signal whose noise is mainly that of the detector. A multiplex measurement like that registered by a Fourier transform spectrometer can improve the SNR, compared to that of a scanning grating spectrometer, of the order of the square root of m, where m is the number of points in the spectrum.

– Jacquinot [JAC 48, JAC 54a, JAC 54b, JAC 60] on the optical throughput advantage or the Jacquinot advantage, which is linked to the intrinsic brightness of interferometers. An interferometer transmits the whole IR radiation that travels through the sample to the detection system. The circular apertures of the interferometer do not limit the illumination of the sample, unlike the slits in a grating spectrometer, which are required for a good resolution. Indeed, the finer the slit, the better the resolution, but in return, IR light is attenuated. The advantage of a Fourier transform spectrometer differs depending on wave number and resolution.

– J. Connes and P. Connes [CON 61a, CON 61b, CON 61c, CON 61d, CON 66] on the advantage of precise sampling through the interference fringes of a laser source, allowing the continuous recording of the measured spectrum; this technique can be used to precisely determine the optical path difference and also the data digitization during the interferogram acquisition. It is important to note that prior to the availability of the first gas lasers, P. Connes used a monochromatic cadmium lamp beam propagating through the interferometer, along the same path as the primary sample beam.

– Finally, Cooley–Tuckey [COO 65] on how Cooley–Tuckey fast Fourier transform (FFT) algorithm can be used to numerically obtain the inverse Fourier transform of the recorded interferogram, taking into account the constraints related to the instrumental line shape, apodization and optimum sampling interval, thanks to the works of J. Connes [CON 61]. The term Fourier transform infrared spectroscopy originated in this mathematical processing required for the conversion of interferogram data into the line spectrum.

FTIR spectrometer is a commonly used term nowadays. This technique is sometimes divided into two phases: the first one involves the recording of an IR spectrum of a sample as an interferogram, and the second one, the IR spectrum calculation by Fourier transform of the interferogram. The commercial brands of instruments such as Brucker, Bomem or Nicolet record the interferogram in numerical form in a file and then the corresponding spectra can be displayed on a screen after numerical Fourier transform by FFT.

1.2.1. *Principle of IR spectrum acquisition by interferometry*

[DAH 21] gives a description of a homodyne monochromatic interferometer using a laser as the source of monochromatic light of wavelength λ. It is made up of a fixed beamsplitter and a compensator, parallel to each other (Figure 1.1). After traveling through the beamsplitter–compensator set, the light beam splits into two paths (r_1 and r_2) and is then reflected by two parallel mirrors, a fixed one denoted by M_1 and a mobile one, denoted by M_2 (Figure 1.1). It can be noted that the rays reflected by M_2 travel through the beamsplitter twice, while those reflected by M_1 go through the beamsplitter once, leading to a phase shift. The compensator thus compensates and symmetrizes the optical paths in the two Michelson arms.

The beam recombined in the beamsplitter–compensator set generates interference fringes on the detector. These are constructive or destructive interference patterns, depending on the path difference Δx between the two rays, depending on the relative position of the two mirrors M_1 and M_2. The intensity can be written as a function of the electrical field E_0 of the radiation, which is as follows:

$$\frac{I(\Delta x)}{\varepsilon_0 c} = \frac{1}{2}\left|\vec{E}_0\right|^2 + \left|\vec{E}_0\right|^2 \cos\left(\frac{2\pi}{\lambda} r_2 - \frac{2\pi}{\lambda} r_1\right) = \frac{1}{2} I_0(\sigma)(1 + \cos(2\pi\sigma n(\Delta x)) \qquad [1.12]$$

where c is the speed of light and ε_0 is the vacuum permittivity.

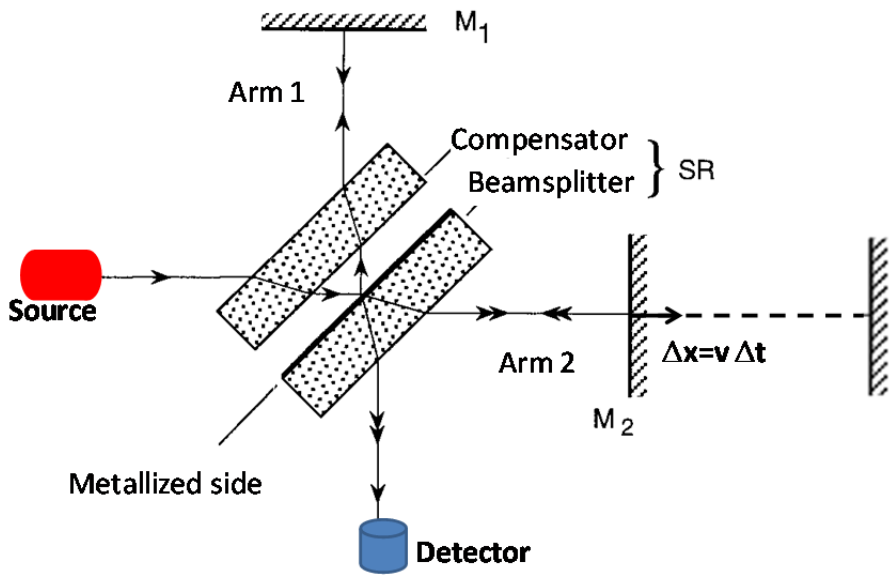

Figure 1.1. *Interferometer diagram. For a color version of this figure, see www.iste.co.uk/dahoo/infrared2.zip*

Interference fringes are formed in the observation plane, coinciding with the detector surface. When the mobile mirror moves, they are transformed into a modulated electric signal that follows the light intensity variations. This signal is directed towards a counter that counts the number of displayed fringes. A fringe is a complete cycle in the variation of light intensity, which passes periodically from a maximum value to zero and then to a maximum value. Each cycle corresponds to a displacement such that $\sigma n\Delta x = 2$. If the path difference Δx corresponding to a cycle and the index n of the surrounding medium are known, the wave number σ or the wavelength λ can be deduced. Conversely, if n and λ are known, Δx can be deduced.

In an interferometer used for studying the spectrum of molecules absorbing light in the IR range, the source used emits a complex polychromatic radiation. If the incident monochromatic flux of wave number σ is denoted by $\phi(\sigma)$, then for a path difference $\Delta = n\Delta x$, the expression of the emergent flux is written as:

$$\phi(\Delta) = \frac{1}{2}\int_0^{\infty} \phi(\sigma)(1 + \cos(2\pi\sigma\Delta))d\sigma \qquad [1.13]$$

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