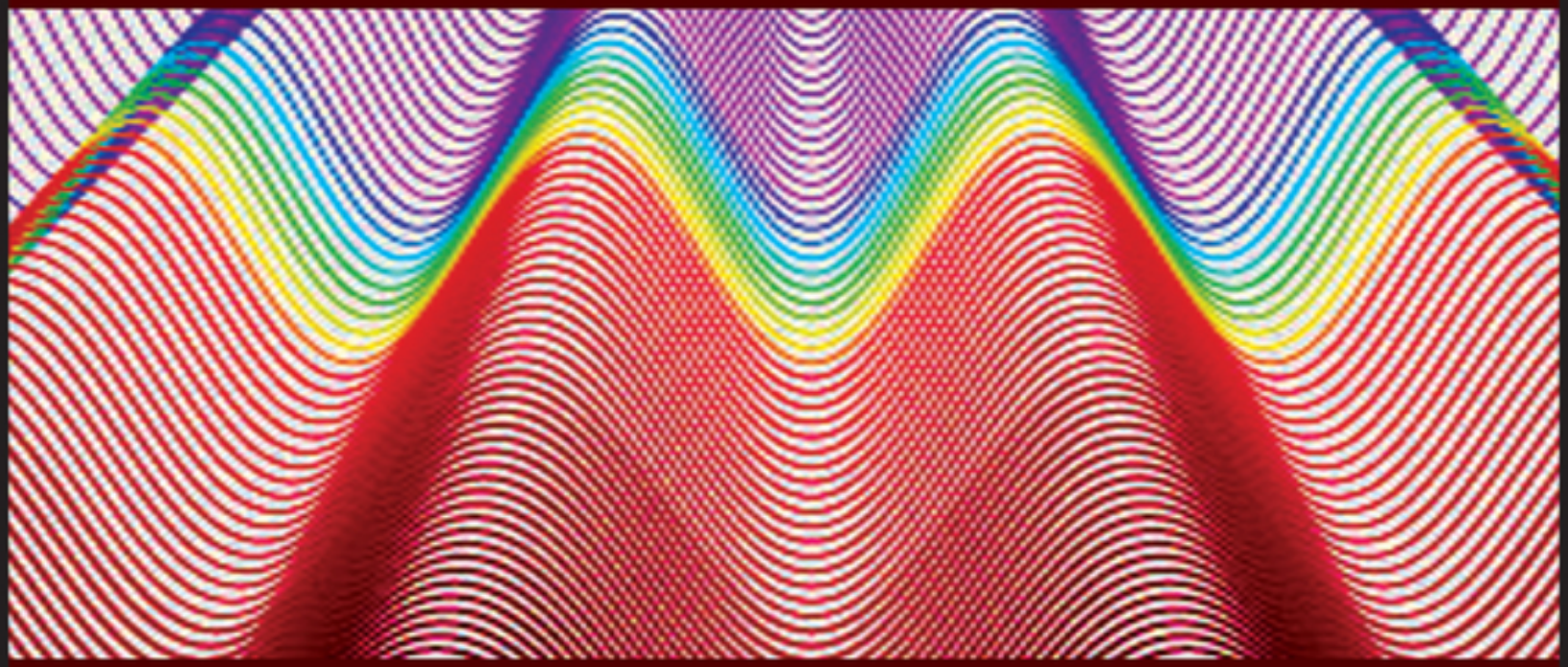
WAVES SERIES

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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Infrared Spectroscopy Set

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.

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

[1.1]

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

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:

[1.2]

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

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:

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

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 $k(\sigma, P)\, l << 1$, 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

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