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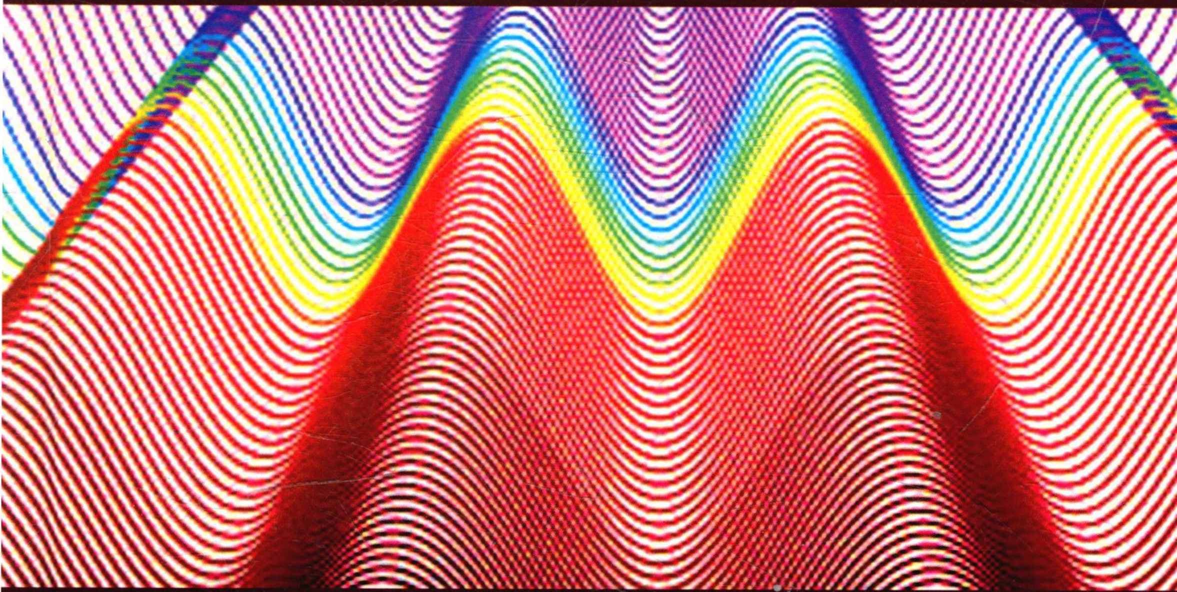

Volume 1

Infrared Spectroscopy of Diatomics for Space Observation

Pierre-Richard Dahoo

Azzedine Lakhlifi

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INFRARED SPECTROSCOPY SET

Coordinated by Pierre-Richard Dahoo and Azzedine Lakhlifi

This book describes different theoretical models developed to identify the near and mid infrared (IR) spectra of diatomic molecules isolated in the gas phase or subjected to environmental constraints, useful for the study of environmental sciences, planetology and astrophysics.

The Van Vleck contact transformation method is presented to complement the standard approach generally applied in the calculation and analysis of IR transitions between vibration-rotation energy levels.

The semi-classical model of Robert and Bonamy, as well as the extended substitution model of Lakhlifi-Dahoo applied to environmental spectroscopy, are described in the framework of the Liouville formalism and the profiles of diatomic lines and their isotopologues subjected to environmental constraints are calculated by applying the cumulant expansion.

The applications presented in this book show how molecular interactions modify the near and mid IR spectra of isolated diatomics under the effect of pressure, a nano-cage (substitution site, Clathrate, Fullerene, Zeolite) or surfaces, to identify the characteristics of the perturbing environment.

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Foreword

Light is one of the vital elements for the living world. Our sun provides us with not only energy but also light, the latter of which reveals the beauty of that which surrounds us, and reveals to us shapes, textures, colors, shadows, reflections, and more. Light also reveals thousands of nuances that enable us to perceive the world around us and that make sight our finest, most developed and most useful sense in everyday life. Even if we are less frightened by it than our ancestors were, the luminous phenomena surrounding us are still as surprising and intriguing. They often seem inexplicable and complex as they are multiple, variable, changing, fast and impalpable.

However, none of this proceeds from magic and can be explained by physical phenomena, most of which have already been interpreted and modeled. The aim of spectrometry is to strive to understand the interactions between light and matter and, by analyzing changes in the color of light before and after interactions, to identify the interacting environment and in particular its composition.

In the atmosphere, an environment characterized by its low density, light allows this analysis to be made from a distance. This particularity has allowed us to improve our knowledge of the environments that surround us; from rainbows caused by drops of water, to the great northern lights, to comet tails, and all the way to distant galaxies. This information enables us to remove ourselves from Earth's attractions and to explore these worlds. The number of exoplanets being discovered keeps on increasing, while a little over 20 years ago, their existence was just speculation and the subject of science fiction.

But the eye is also a limited detector and particularly so for the infrared range. Yet this range of frequency has its own assets in both our everyday life as well as for scientists. It enables us to switch on the television with a remote control, but also, for more technical applications, to analyze numerous chemical species and to give information on the speed of objects, their temperature and many other parameters.

Today, this field of application is far from being an exhausted and perfectly mastered science, but some fabulous progress has been made over the last decade. This knowledge and simultaneously the possibilities opened for space exploration has permitted some considerable scientific advancement. Harnessing these advances has allowed us today to further our understanding of our atmosphere and our exploration of the worlds surrounding us, even those we cannot see, or cannot imagine. This knowledge is essential for the modern explorers that we are, whose utmost aim is directed toward improving the description of these worlds thanks to teledetection.

Capitalizing and gathering this knowledge is therefore an endeavor that is necessary for pursuing our quest for knowledge. Beware, delving into these phenomena may cause vertigo. Physics and chemistry combine on the molecular, atomic, electronic, photonic, etc. scales. Mastering them will enable you to understand the fundamentals of physics, and to develop more and more sophisticated instruments and methods to extract multiple useful pieces of information from radiation. This information will turn you into the sorcerers of tomorrow, capable of decoding physical–chemical processes via light.

Philippe KECKHUT
Versailles Saint-Quentin-en-Yvelines University
and Director of LATMOS

Preface

Theoretical and instrumental spectroscopies optimize the parameters that enable chemical species, molecules, radicals and ions to be characterized based on theoretical models and experimental data. The results of research undertaken in laboratories are used to analyze the data provided by different instruments used in astronomy for observing the sky or space and detecting atoms, molecules or chemical species (ions, radicals, macromolecules, nanocages, etc.) located in different environments ranging from the atmosphere of planets, including Earth, and their satellites to interstellar media, comets and exo-planets.

Continuous progress within the field of the technology of embedded and communicating systems enables a mass of data to be retrieved with greater and greater precision (high-resolution spectra, weak signal-to-noise ratio of more and more effective detectors, more reliable transmission and data-retrieval techniques) from instruments implemented in observatories based on the ground or in space probes and space-borne telescopes. Thanks to sky-viewing telescopes or telescopes coupled with measuring instruments, spectrographs, spectrometers and interferometers equipped with standard detection systems or more sophisticated ones, using, for instance, intensity autocorrelation or heterodyne detection techniques, many discoveries and advances in astrophysics have been made possible. For example, without being too exhaustive, one can list some of the following advances from space observation:

– Galileo Galilei, who was one of the first astronomers to have used a telescope (a word he invented in 1611) for observing the sky and the stars. In his writing concerning his observations, his discovery in 1610 that four moons revolve around Jupiter led him to adopt the heliocentric model of the universe, as proposed by Copernicus in 1543 against the geocentric model, which was taken for granted under the authority of the scientific community and the church;

– in an article in 1919, F.O. Dyson, A.S. Eddington and C. Davidson used Eddington's photographs taken during a solar eclipse as the basis for presenting the determination of a star's light deviation by the Sun's gravitational field. These findings then confirmed the gravitational field as predicted by Einstein's theory of relativity;

– later, in 1929, the expansion of the Universe was discovered by Edwin Hubble, on the basis of the redshift (Doppler effect) of the galaxies from the spectrum of Cepheids and stars analysis characterized by variations in brightness, observed in the Hooker telescope of the Mount Wilson Observatory in California;

– by improving observation apparatuses, in 1956, Handbury Brown and Twiss used the autocorrelation technique with an intensity interferometer to measure the angular diameter of the Sirius star in the optical range;

– in 1965, fossil radiation or cosmic microwave background radiation (CMBR), predicted by Ralph Alpher in his thesis in 1948, was discovered by Arno Penzias and Robert Wilson at the Bell Telephone Laboratories when developing a new radio receiver after interferences were detected, regardless of the orientation of the antenna being constructed and corresponding to 3.5 K in temperature for a wave length of 7.35 cm;

– in 1976, M.A. Johnson, A.L. Betz, R.A. McLaren, E.C. Sutton and C.H. Townes observed a mesospheric emission in a non-local thermodynamic equilibrium system ("non-LTE") coming from Mars as well as Venus. This phenomenon, which was discovered for the first time, was later interpreted as a CO_2 stimulated emission in the infrared region around 10 μm by D. Deming and M.J. Mumma in 1983;

– in 1990, J.C. Mather *et al.* determined the characteristic CMBR temperature value to be at 2.735 K based on data transmitted by COBE ("cosmic background explorer") satellite launched in 1989, equipped with FIRAS ("far infrared absolute spectrometer") an instrument that measured the fossil radiation spectra of the cosmic microwave background more precisely;

– in 1995, a planet around a solar-type star, 51 Peg b was observed for the first time by Mayor and Quelozà of the Hautes Provence Observatory (OHP), using the Doppler effect measurement of the spectrum obtained with the Elodie spectrograph following the periodic variations of the radial speed of the host star at 56 m/s in 4 days;

– using a new type of vacuum cross-dispersion spectrometer, in 1999 P. Connes and F. Bouchy discovered, again at OHP, another exo-planet around the star Upsilon Andromedae with a measurement accuracy of 3 m/s;

– and very recently, on September 14, 2015, LIGO ("Laser Interferometer Gravitational-Wave Observatory"), detected distortions caused by gravitational waves in space time for the first time. This phenomenon which was predicted by Einstein's theory of general relativity, was generated by two black holes that collided at about 1.3 billion light years.

A special mention should be made about Rosetta, the spacecraft on the ESA mission, with contributions from the EU Member States and NASA. It was placed into orbit around the comet of the Jupiter 67P/Churyumov-Gerasimenko (67P) of the Jupiter family. Comets are the best sample of primitive solar nebulous material currently available and which date back 4.57 billion years to the origin of our planetary system. Rosetta found the comet's nucleus on August 6, 2014, at 3.7 astronomical units (AU) from the Sun, and landed the Philae spacecraft on the surface of the nucleus on November 12, 2014, when the comet was at 3.0 AU from the Sun.

The initial observations enabled:

– a reference frame to be made that described the global shape, morphology and composition of the surface, as well as the global physical properties of the nucleus;

– various molecules to be detected, including $H_2{}^{17}O$, $H_2{}^{18}O$, CO and CO_2, and for their temporal variability, as well as their heterogeneous distribution to be evaluated;

– the measurement of the high D/H ratio in water, 5.3×10^{-4}, which excludes the hypothesis that comets from the Jupiter family only contain ocean water from Earth.

The Rosetta mission started exploring our origins because of the efforts of thousands of people at ESA, at NASA, in the industry, in space agencies and of engineers and scientists all over the world in different research and observation centers.

Telescopes are continuously being improved to investigate the origins of the universe and to search for other worlds outside our own. The James Webb space telescope at NASA, the successor of the Hubble space telescope and whose launch is planned for 2018, will allow us to better ascertain the origins and evolution of galaxies. The mission of the "European Extremely Large Telescope", which should be completed in 2024, is to observe exo-planets, the first days of the universe, the supermassive black holes and the mysterious nature of dark matter and dark energy. E-ELT, James Webb and other next-generation telescopes will also attempt to search for planets similar to Earth in other solar systems, as well as observing and studying their atmospheres, orbits and origins.

All of these instruments are sent into space for exploring galaxies and the universe and are equipped with sensors and other detection systems specifically designed for the electromagnetic radiation used for closer probing of the environment to be studied. On Earth, technologies of connected objects associated with Drones will increase our observation capacities. These evolutions participate in the phenomenon of "Big Data" and, for reliable data analysis, it is necessary to fully grasp the physical models developed in order to identify from their spectral signatures, the diatomic or polyatomic molecules present in the environment being probed. First, spectroscopy enables the structure of chemical species (in gas, liquid or solid phases) to be determined by applying the methods and tools of theoretical spectroscopy, and species (atoms, molecules, molecular fragments, radicals, etc.) to be identified in different environments (nanocavities, environments containing different species, ice surface, dust surface, etc.). Using these species themselves as probes for characterizing the environment (temperature, pressure, composition) and its nature from a correct analysis of collected data requires theoretical models that have been specifically developed, given the astronomic conditions that prevail in which the densities of the species are very weak and the temperatures very high or very low, depending on the probed medium.

The theoretical models are supported by the fundamental laws of physics and are developed according to a bottom-up approach. For an objective prediction, one can deduce the consequences that arise from the model based on realistic hypotheses and the equations hence derived from the application of the known physical laws. One can also depart from the experimental methods and use a top-down approach to build an experimentation database based on the studied system's response to external constraints, which can either be natural, prevailing *in situ* conditions, or else purposely applied. Then from experimental results and observations, an analysis based on empirical models built on physical grounds can be proposed. The models can be resolved analytically or digitally. When it is possible to implement the experimentation, the simulation results can be compared to the experimental ones and interpreted using the theoretical or empirical models and by applying an inverse method to fit the experimental data with the theoretical ones for comparison. This is achieved by defining a cost function that is used to minimize the difference between theoretical and experimental results by adjusting theoretical parameters through a least square procedure based on the linear Nelder–Mead simplex or nonlinear Levenberg–Marquardt or BFGS algorithms, which allows molecular constants to be determined, for instance.

This book describes the theoretical methods that are applied within the context of fundamental research for interpreting the spectra of diatomic molecules observed in the infrared region when these molecules are subjected to an environment where the temperature and pressure modify their infrared spectra in the gas phase or in nanocages. Many reference textbooks discuss spectroscopic studies of diatomic molecules in the gaseous phase at different temperatures. In this book, we will describe the theoretical models that have been developed for studying the modification of infrared spectra of diatomic molecules under the effect of pressure, resulting in the broadening of line widths or their shifts at the center or the modification of the rotational–vibrational spectra as a result of nanocages or surface effects.

This book is intended for master's or doctorate students, teachers and researchers or astronomers and astrophysicists who analyze the data corresponding to the interaction of the electromagnetic radiation with the matter in the infrared region in order to identify chemical species and their environments.

The manuscript is divided into three parts: the first, which comprises two chapters, deals with well-known theoretical models of diatomic molecules and which are described in many standard textbooks that deal with the spectroscopy of an isolated diatomic molecule to be described; the source of this part is in well-known publications such as those of Herzberg, Wilson, Amat, Nielsen and Tarrago, Barchewitz, Hollas, Lefebvre-Brion and Field, Brown, Landau, Cohen-Tannoudji or Messiah. The list would be too long and mention is only made of those who were consulted for this part, to which we should add G. Amat's Molecular Physics course at Master 2 level at UPMC and the courses of J.M. Flaud and C. Camy-Peyret in second year master's (Master 2 level) degree in DEA (Diplôme d'Études Approfondies) Laser and Matter at UPSUD. The second part, which also comprises two chapters, describes the theoretical models developed in the research field and applied to the analysis of experimental results in the CNRS laboratories, a national research center in France. These works were initiated particularly in the Molecular Physics group of Besançon (L. Galatry, D. Robert, J. Bonamy, L. Bonamy, C. Girardet, A. Lahklifi, etc.) and later collaboratively pursued with laboratory researchers in the region of Paris (C. Boulet, J.M. Hartmann, P.R. Dahoo, etc.) to study molecules in different media and subjected to interactions whose effects, particularly on the nanometric scale, modify the IR spectral signature of the molecules. Finally, in the third part, we introduce some applications of the models described in the second part to study some diatomic molecules.

Chapter 1 deals with diatomic molecules in general, giving the full Hamiltonian operator, which enables us to determine their different electronic states and, within the framework of Born and Oppenheimer approximation, their vibration–rotation states. The symmetry properties of homonuclear and heteronuclear molecules, as well as the nomenclature of the different electronic levels of vibration–rotation degrees of freedom based on the corresponding symmetry groups, are also recalled. Chapter 2 introduces the models developed for studying, in the near and mid infrared ranges, the vibration spectroscopy of a diatomic molecule in its fundamental electronic state. Also described are the Rayleigh–Schrödinger's standard perturbation theory and the non-standard contact perturbation theory proposed by Van Vleck for determining the states of vibration when one considers the non-harmonicity of the electronic potential driving the movement of the nuclei. Theories for calculating the states of rotation in the far IR range are also addressed, as well as the effect of coupling between the vibrational and rotational degrees of freedom on the corresponding spectra. Chapters 3 and 4 remind the reader of the theories developed for analyzing the spectra of diatomic molecules when they are in a constrained environment, under the effect of pressure in gas phase or in nanocages in condensed media. The Liouville theorem in the Liouville line space and the linked cluster theorem through the cumulant expansion, particularly developed in the field of statistical physics, are applied to study the effect of interactions between the active molecule and its environment in a system characterized by large degrees of freedom. The shifts and widths of lines are calculated as well as the modifications of the spectra, particularly those connected to the rotation in the condensed phase. In Chapter 5, the theories described in previous chapters are applied to different types of diatomic molecules to illustrate how the different applications allow the spectra observed in Raman spectroscopy with a lidar, in classical absorption spectroscopy, to be analyzed and interpreted when the molecule is in gas phase under pressure, in a nanocage, or on a surface.

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September 2017

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