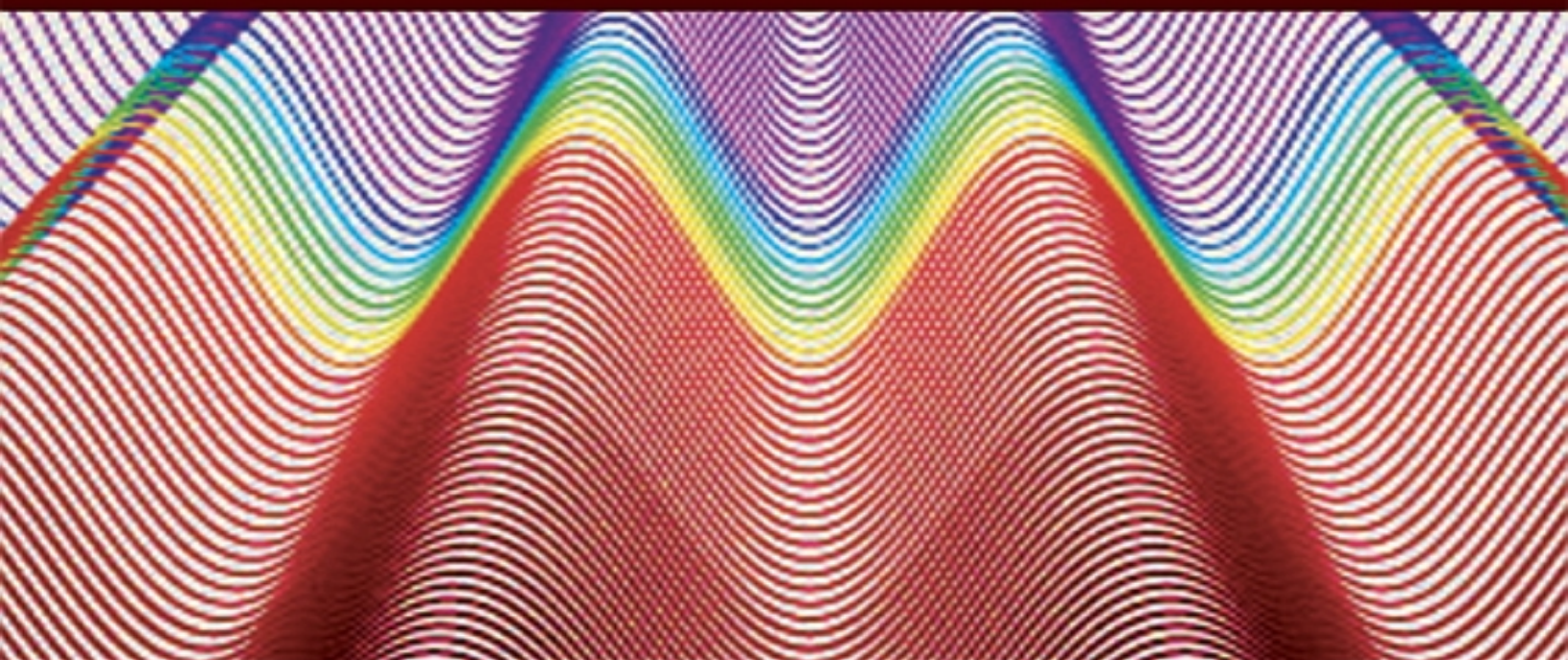


WAVES SERIES
INFRARED SPECTROSCOPY SET



Volume 3

**Infrared Spectroscopy
of Symmetric and Spherical
Top Molecules
for Space Observation 1**

**Pierre-Richard Dahoo
Azzedine Lakhli**

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Infrared Spectroscopy of Symmetric and Spherical

coordinated by

Pierre Richard Dahoo and Azzedine Lakhli

Volume 3

Infrared Spectroscopy of Symmetric and Spherical Top Molecules for Space Observation 1

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Foreword

Before the early 1950s, the immensity of the cosmos seemed essentially cold and barren. The launch of Sputnik 1 on October 4, 1957, marked the beginning of the space age, and soon afterwards automated space explorers were sent through the solar system and orbiting terrestrial observatories were launched. At the same time, the development of advanced detection techniques and increasingly powerful telescopes contributed to the unprecedented rapid expansion of terrestrial observatories. All these developments led to a radical transformation of our view of both planetary atmospheres and interstellar medium, revealing an unexpected molecular abundance and giving birth to a new discipline: astrochemistry.

This transformation relies heavily on the use of light as a messenger, providing information on the composition of these media by taking advantage of the available range of wavelengths. Indeed, although Newton understood the decomposition of visible light as early as 1666, it was not until 1800 that Herschel broadened our view with the discovery of infrared radiation, followed shortly by Ritter's discovery of ultraviolet radiation, and then Röntgen's 1895 discovery of X-rays. Then, Maxwell unified these various radiations in his electromagnetic field theory. Starting with the 1920s, the development of quantum physics by Heisenberg, Schrödinger, Pauli, Dirac, etc. brought the tools to understand why chemical elements (atoms and molecules) left a discrete signature, in the form of absorption or emission lines in the electromagnetic spectra, an observation that Wollaston and Fraunhofer had made over a century earlier. This laid the basis for the use of spectroscopy as an essential analytical tool.

Nevertheless, since molecules mainly absorb short wavelength radiation, infrared and microwave radiations, largely absorbed by the Earth's atmosphere, the advent of space observatories was decisive for astrochemistry. However, observatories in the microwave range were also set up at the ground level, at high altitude and very dry regions (ALMA), or airborne (stratospheric balloons, SOFIA). The astrophysicists now have a significant array of instruments available that are dedicated to spectroscopy, which obviously includes spectrometers airborne by space probes heading for Venus (Venus Express), Mars (Mars Express, TGO, etc.), Jupiter (Juno), Saturn (Cassini-Huygens), comets (Rosetta), etc. An exciting future lies ahead in this field, given the terrestrial observatories (E-ELT, etc.), space observatories (JWST, WFIRST) and various planetary missions.

Moreover, the discovery in 1995 by Mayor and Quéloz (Nobel Prize in Physics 2019) of the first exoplanet, and the exponential number of discoveries of these celestial bodies ever since, opened the way for conducting the very first spectroscopic studies of their atmospheres. The coming new space instruments (JWST, ARIEL) will even be partially or entirely dedicated to the spectroscopic characterization of these extrasolar planets, the target being the research of biosignatures.

However, using all these instruments and their large amounts of data requires significant upstream experimental and theoretical laboratory work, in order to record and model the spectra of many molecules. This may involve relatively complex organic molecules as well as simple molecules. Indeed, contrary to a preconceived idea, there is definitely still not enough modeling of the infrared spectrum of "small" molecules (CO_2 , H_2O , CH_4 , NH_3 , etc.) in the current databases. In fact, the data needed by planetologists nowadays need to cover "extreme"

conditions that were to a little extent, if at all, studied in the laboratory, that is: very high temperatures and pressures, molecules in confined environments, etc.

The aim of this book is to review the theoretical knowledge required for understanding and modeling the spectra of two molecules that are essential in planetology, ammonia (NH_3) and methane (CH_4), and to provide the tools for their spectroscopic study in a confined environment, such as the clathrates.

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January 2021

Preface

Infrared (IR) spectroscopic analysis is of fundamental interest for understanding the physics of the atmosphere and planets, as well as for the study of observable molecules in astrophysics. In the space field of space sciences or exploration, observations conducted by means of instruments at the ground level, or airborne by space probes or space telescopes, contribute to the discoveries that drive science forward or participate in observational sciences. The resulting database enables the confirmation or clarification of theoretical predictions that improve our understanding of the physical and chemical phenomena and processes in the surrounding environments. These observations are facilitated by technological advances and progresses both in the implementation of detection systems and in the analysis conducted by increasingly high-performance computers using ever better controlled statistical methods or theoretical models for the analysis of observational data. A recent example of black hole observation is worth mentioning:

The Event Horizon Telescope (EHT) is a large telescope array consisting of a global network of radio telescopes and the EHT project combines data from several very-long-baseline interferometry (VLBI) stations around Earth with angular resolution sufficient to observe objects of the size of a supermassive black hole's event horizon.

The authors collaborating on the EHT project apply the methods that rely on the interference of electromagnetic waves using an array of instruments located at various sites on the Earth's surface. The methods applied are increasingly sophisticated and require international

collaborations for data collection, analysis and development in order to reveal the observed phenomenon.

The diversity of discoveries contributes to advances in the field of astrophysics and cosmology, building a better understanding of the phenomena at the origin of the universe and addressing the nature and distribution of its constituents that are currently considered to be composed of below 5% visible matter, about 25% dark matter and 70% dark energy, which is responsible for a force that repels gravity and is believed to contribute to the expansion of the universe. Thanks to the analyzed data from space observations, astronomers and physicists have to improve the theoretical approaches, among which the following are worth mentioning: the cosmological model and Einstein's equation in the general theory of relativity or the geometric theory of gravitation published in 1915 [EIN 15], and baryogenesis as an interpretation of the predominance of matter over antimatter [SAK 67].

Similarly, using automated and connected instruments, such as that of the Mars Perseverance Rover 2020 which was successfully launched on July 30, 2020, planetary exploration programs pave the way for observations and data analysis whose interpretation requires theoretical models adapted to various ranges of the electromagnetic spectrum, including IR spectroscopy, which is the focus of this volume.

Theoretical and experimental spectroscopies contribute to the development of methods and devices for the observation and analysis of spectra corresponding to chemical species, molecules, radicals and ions in specific environments, as shown in Volumes 1 and 2 of the set *Infrared Spectroscopy* [DAH 17, DAH 19]. In the IR range, various types of instruments can be used for space observation, in order to detect molecules or chemical species (ions, radicals, macromolecules, nanocages, etc.)

present in the atmosphere of planets, including the Earth, and their satellites, as well as in interstellar media, comets or exoplanets.

In molecular physics, the rovibrational energy levels of a molecule are calculated using the molecular Hamiltonian established by Wilson and Howard [WIL 36], reformulated by Darling and Dennison [DAR 40] and later simplified by Watson [WAT 68]. The contact transformation introduced by Van Vleck [VAN 29] is applied to determine the levels of vibration-rotation energy at different orders of approximation. The formalism of this method is described in Volumes 1 and 2, and its application is illustrated on diatomic and triatomic molecules. It was initially applied by Schaffer *et al.* [SCH 39a] and further improved by Nielsen, Amat and Goldsmith [AMA 57a, AMA 57b, AMA 58, GOL 56, GOL 57, NIE 51]. This method makes it possible to regroup the Hamiltonian in interacting polyads with the application of unit transformations, leading to a matrix form in blocks which is easier to diagonalize. Based on the method proposed by Watson [WAT 67, WAT 68b, WAT 68c] for the theoretical study of isolated states, Flaud and Camy-Peyret [FLA 81, FLA 90] showed that symmetry properties of nonlinear triatomic molecules (H_2O , O_3 , etc.) can be used to build unitary transformations, leading to the transformation of the initial Hamiltonian into interacting blocks that could be linked to the experimental observations of interacting vibrational levels. Using similar methods developed in the field of IR spectroscopy, a study of ammonia and methane molecules in molecular physics was conducted by the research groups at the CNRS (French National Center for Scientific Research) laboratories in Paris and Dijon. The results obtained by these groups were shared in the PhD theses conducted in this field. The theses referred to in this volume are included in the references section. In particular, it is worth

mentioning the theses of Moret-Bailly, Tarrago, Champion, Gherissi, Loëte, Coudert, Coquart, Boudon, Gabart and Permogorov [MOR 61, TAR 65, CHA 78, GHE 79, LOË 84, COU 86, COQ 94, BOU 95, GAB 96, PER 96], which are dedicated to the analysis of gas phase spectra and cover both cold and hot bands or combinations thereof. In this work, which is dedicated to the effects of an environment on the spectrum of an NH_3 or CH_4 molecule, as an example of symmetric or spherical tops, the cold bands are only addressed in situations where the degree of rotation is hindered either by a weak coupling (rotational motions limited to weak values of J) or a strong coupling (librational motions) depending on the type of environment, as studied in the theses of Abouaf-Marguin, Dubost, Gauthier, Boissel, Lakhli, Brosset and Dahoo [ABO 73, DUB 75, GAU 80, BOI 85, LAK 87, BRO 93, DAH 96].

As mentioned in the preface to Volumes 1 and 2, the application of methods and tools of theoretical spectroscopy initially developed in molecular spectroscopy for the gas phase and adapted to environments in which the motion of the considered molecule is perturbed makes it possible to not only determine the structure of chemical species (in the gas, liquid or solid phase), but to also identify the species (atoms, molecules, molecular fragments, radicals, etc.) in various environments (nanocavities, media containing various species, ice surface, dust surface, etc.). The species themselves can be used as probes in order to characterize the environment (temperature, pressure, composition) and determine its nature based on theoretical models developed for the analysis of corresponding data.

This book describes the theoretical methods developed in the framework of fundamental research for the interpretation of the spectra of ammonia molecules, which are characterized by a ternary axis of symmetry, from

observed spectra in the IR range when these molecules are subjected to an environment in which the temperature and pressure modify their IR gas phase spectra or in nanocages. It describes the theoretical models for the study of ammonia and methane molecules in these media based on the theoretical models elaborated for the gas phase. The modification of the IR spectra of these molecules can also be interpreted, such as the shift of the band centers or the modification of the rovibrational spectrum in nanocages or on surfaces.

This book is intended for students at master and doctoral levels, teaching academics and researchers, astronomers and astrophysicists who analyze the data derived from the interaction between electromagnetic radiation and matter in the IR range, in order to identify the chemical species and their environments.

This book (Volume 3), which will be followed by a complementary book on applications (Volume 4), presents, to both beginners and experts in the field of spectroscopy, the methods developed through theoretical models using group theory for rigid and non-rigid molecules characterized by the tunneling effect phenomenon and large amplitude motions. Simulations of these models enable the analysis of IR data and the identification of molecules based on transitions and profiles not only in the gas phase from fundamental bands but also when they are forced to evolve in an environment that can be a nanocage or a surface.

Ammonia and methane molecules are members of the class of the molecules with a ternary and quaternary axis of symmetry. The first part is organized into two chapters concerning the symmetry and the use of group theory for the study of symmetric and spherical tops, as well as a review of the line profile of molecules that evolve in

nanocages or on surfaces. Then the theoretical models elaborated for the study of vibration-rotation spectra of polyatomic molecules in the gas phase are briefly recalled as developed in molecular physics. They allow the study of both cold and hot bands, as well as the combination bands, and have been extensively described in the books devoted to the spectroscopic study in the gas phase.

In this volume, the theoretical description only covers the study of cold bands, whose spectra result from transitions from the fundamental vibration-rotation level. The IR spectroscopic study concerns the libration or hindered rotation movements that result from a strong coupling with the environment and the constrained rotational movements when the coupling with the environment is weak (rotation at low J).

The theoretical part resulted from molecular physics was partly inspired by the molecular physics lectures given in the 2nd year of master degree studies by G. Amat at the UPMC and those of J.M. Flaud and C. Camy-Peyret in the master degree of advanced studies, "Laser and Matter", at the UPSUD, and the research works conducted at the CNRS laboratories (Paris, Orsay, Dijon, Grenoble and Reims), which are available particularly in the form of (PhD) theses on spectroscopic studies of symmetric or spherical top molecules in the IR range. The theoretical models specific to research work on the effects of an environment have been developed, particularly in the group of molecular physics in Besançon (L. Galatry, D. Robert, J. Bonamy, L. Bonamy, C. Girardet, A. Lahklifi, etc.), in order to analyze observations on molecules subjected to pressure or isolated in condensed phase media in collaboration with researchers from Paris and Orsay (L. Abouaf, H. Dubost, B. Gauthier, J.P. Boissel, P.R. Dahoo, etc.)

These models are applied to study the molecules subjected to interactions in various media, whose effects manifest particularly at the nanometer scale, which modifies the profile of the IR spectra of these molecules. The theoretical inclusion model or the extended model proposed by Lakhlifi and Dahoo was explained in Volumes 1 and 2, and certain programs for the numerical calculation were described in these volumes, mainly in Volume 2. They are used to calculate the IR spectra of molecules in nanocages.

[Chapter 1](#) describes the main tools and methods developed in group theory and tensor algebra for their applications and IR spectroscopy. The finite and continuous point symmetry groups allow for classifying the energy levels associated with electronic, vibrational and rotational degrees of freedom by their symmetries connected to an irreducible representation of the group. The exchange of identical nuclei in a molecule, where tunneling inversion can be observed through experimentation, is studied as part of the permutation-inversion group.

In [Chapter 2](#), group theory methods are applied to determine the symmetry groups of symmetric top molecules with reference to the NH_3 molecule and the spherical top molecules with reference to the CH_4 molecule. The isotopologues (the hydrogen atom H is replaced by the deuterium atom D) of these molecules are also studied from the point of view of symmetry groups. The symmetry properties of NH_3 and CH_4 molecules and their isotopic varieties are presented in this chapter and their geometric symmetry groups are determined. It is shown that the loss of a symmetry element modifies the symmetry group from a more symmetric group to a less symmetric one, and consequently modifies the observable IR spectra. The theory of permutation-inversion groups is also applied to determine the corresponding CNPI groups.

In [Chapter 3](#), the group theoretical methods are applied to determine the functions that generate irreducible representations of the symmetry group of symmetric top molecules and spherical top molecules by referring to NH_3 and CH_4 molecules and to their isotopes for various degrees of freedom, either electronic, vibrational, rotational and electron and nuclear spins. An approximate Hamiltonian is used, which makes it possible to express the total wave function as a product of wave functions by neglecting the vibration-rotation interaction. The statistical weights of the levels are calculated by applying the generic formula given by Landau, and the inversion phenomena is described in the molecular symmetry group following the approach of Bunker and Jensen. The various expressions used to calculate a line profile observable in a spectrum, as well as the method used to determine the selection rules in general, are recalled. By neglecting the couplings, the product form of the total wave function that describes the molecule in the zeroth-order approximation and its symmetry properties are taken into account. The objective is to identify the types of symmetry of the energy levels of each type of degree of freedom, and to determine the allowed transitions that give the selection rules in absorption, emission or diffusion spectroscopy. These transitions are the fingerprint of the molecule when it interacts with light in the studies of IR absorption, emission spectroscopy and Raman spectroscopy.

In [Chapter 4](#), the theoretical model developed for the study of IR spectra that result from transitions between the levels of vibration-rotation energy of symmetric top molecules is described with reference to the NH_3 molecule. The resolution of the Schrödinger equation gives eigenvalues of the molecular system that depend on the degrees of freedom of the nuclei and of the electrons in the molecule that do not have simple analytical solutions. An

approximate Hamiltonian is built in the Born and Oppenheimer approximation in order to decouple the rapid motion of electrons from that of nuclei. For each electronic state, the Hamiltonian of nuclei can be used for the study of vibration-rotation motions of the molecule. The various steps in the calculation of the vibration-rotation energy levels are explained in the applications of quantum mechanics applied to molecules. The decoupling of the translation motion from the other degrees of freedom is achieved by studying the vibration-rotation motion in a reference frame attached to the equilibrium configuration of the molecule (mobile reference frame) whose origin coincides with its center of mass (Eckart-Sayvetz conditions). The vibration is then studied in the approximation of low amplitudes. A partial decoupling is achieved between the vibration and rotation motions of the molecule. The Van Vleck contact method is used for splitting the Hamiltonian into blocks, in order to study the IR spectra of the molecules. The transitions between the energy levels resulting from the interaction between the dipole moment or the induced dipole moment of the molecule and the IR electromagnetic radiation lead respectively to the absorption and/or emission spectra of the molecule or to the Raman spectra of the molecule.

In [Chapter 5](#), the theoretical model developed by the spectroscopic group of Dijon in France is illustrated with reference to the methane molecule (CH_4), a spherical top, in the gas phase. The theoretical study of this molecule is not easy. In our opinion, the Dijon approach appears to be the most complete, though it relies on a difficult mathematical formalism. Group theory methods are applied within the framework of the tensor formalism developed in Dijon. More than one chapter would be needed in the case of spherical tops, in order to tackle the various theoretical models elaborated for the calculation of the energy levels

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