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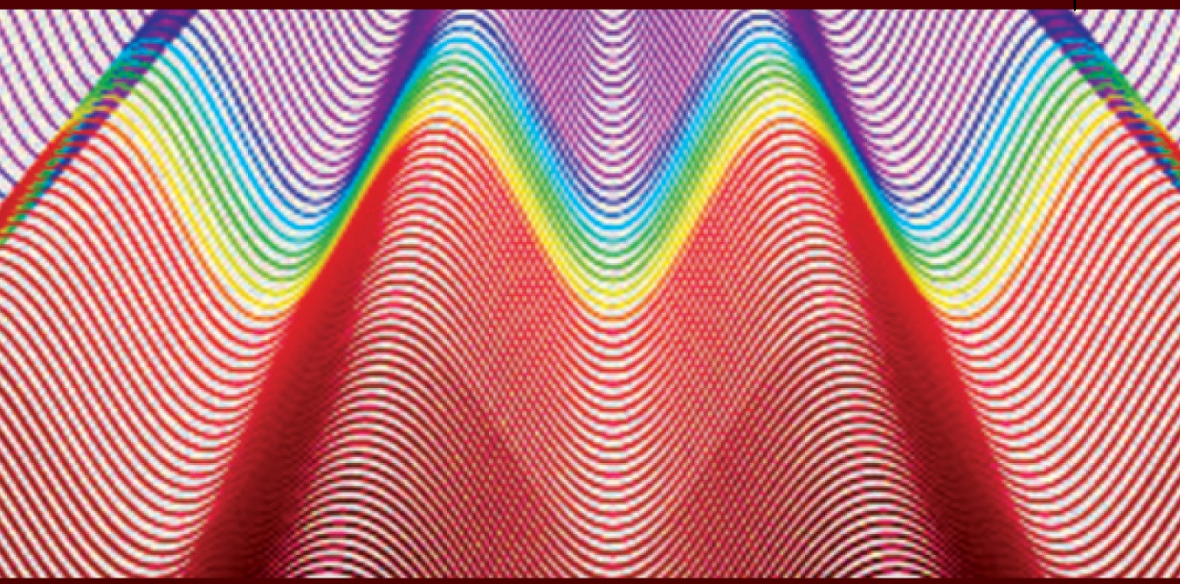

Volume 3

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

Pierre-Richard Dahoo
Azzedine Lakhlifi

ISTE

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coordinated by
Pierre Richard Dahoo and Azzedine Lakhlifi

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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, Lakhlifi, 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 and the

transitions between these levels. An outline of the model is given to study methane spectroscopy in the gas phase. Based on this theoretical model, applied to the lowest level in the vibration–rotation expansion, the effect of an environment on the spectroscopic characteristics of methane CH_4 can be studied when it is embedded in various media, based on the symmetry considerations as presented in the first two chapters. Its application is illustrated on the dipole moment for the IR spectroscopy transitions of methane in the gas phase.

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January 2021

1

Group Theory in Infrared Spectroscopy

This chapter reviews the use of group theory methods for the study of a molecule using infrared (IR) spectroscopy. The application of group theory involves the use of character tables in the theory of representation of a point symmetry group associated with a molecule. The focus is on the elements of the theory of representation, which are used in the following chapters for the study of ammonia (NH_3) molecules (an example of a symmetric top), and methane (CH_4) (an example of a spherical top), and their isotopologues. Elements of the tensor operator algebra are also reviewed for the study of CH_4 within the framework of tensor formalism. The permutation-inversion group CNPI is also presented with reference to NH_3, in order to distinguish between the symmetry group based on the geometry of the molecule, i.e. on its symmetry elements, and the permutation group of the identical nuclei.

1.1. Introduction

The point symmetry group of a molecule reflects the geometric form of the molecule. It is well adapted to the Hamiltonian of Schrödinger's equation, the energy operator which is the sum of the kinetic energy operator and the potential energy operator of the molecule, since it is built on space variables of the position of the electrons and nuclei. When the transformations involving identical nuclei exchanges are taken into account, the point symmetry group is not adapted to the study of the symmetries of the wave function which includes quantum variables related to the spins of identical nuclei when describing a vibration–rotation state for a given electronic state. The identical particle permutation group, which is the symmetric group S_n (not to be confused with the point group S_{2n}) of permutations of n identical particles of order $n!$, is more appropriate.

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First Edition. Pierre Richard Dahoo and Azzedine Lakhlifi.

Molecules characterized by a potential energy function with several minima are not rigid molecules. To take into account the inversion in the case of semi-rigid molecules such as NH_3 and its isotopic varieties, a group of higher order that has the irreducible representations needed to list the irreducible representations used for the classification of the molecule wave functions depending on the Hamiltonian symmetry properties has been used. This group is built from the permutation-inversion group that takes into account situations in which inversion can be observed through identical nuclei exchange in the molecule [BUN 98, HOU 62, HOU 63, HOU 65, LON 63].

1.2. The point-symmetry group of a molecule

The point-group theory applies to rigid molecules, in the sense that the motions of nuclei during a vibration are described by low-amplitude motions and the rotation of the molecule as a whole is described within the framework of rigid rotators (see section 2.2). The construction of the point group relies on the geometric form of the molecule. The operators associated with the elements of a point symmetry group l of a molecule generally commute with one part of the exact or full Hamiltonian (energy operator of an effective Hamiltonian) of the molecule (at the zeroth-order approximation). The focus is on the space position variables of the electrons and nuclei and on the Schrödinger equation for vibration–rotation for a given electronic state.

In this case, the complete nuclear permutation-inversion (CNPI) group [BUN 98, HOU 62, HOU 63, HOU 65, LON 63] is built from a permutation-inversion group (see section 1.6). The elements of this group are the permutations of identical nuclei of a molecule (group of permutation S_n) and the group built on the operator whose effect is the inversion of all the coordinates of nuclei and electrons. This group operates on the exchange of nuclei independently of the observable geometric form. There is a direct link between the symmetry properties of the Hamiltonian and the operators of this group, while the link with the operators of the point symmetry group is indirect. It is worth noting that in some textbooks dedicated to group theory applications, the construction of double symmetry groups is explicitly presented [BUN 98, HAM 62, LAN 75, WIL 55] by building a higher-order group by tensor product of the point symmetry group with a second-order group built on the space coordinate inversion operator. This approach was initially proposed by H. Bethe [BET 29], who used group theory to interpret the degeneracy lifting of atomic orbitals of atoms inserted in crystallographic sites. His work was based on the effect on spin variable symmetry linked to the irreducible representation of a double group. For the structures that were not addressed by Bethe's and Opechowski's approach

[OPE 40], which showed that the classes of a double group G^* built with G, a subgroup of the three-dimensional rotation group SO(3), could be less than twice the number of G classes.

1.2.1. *Symmetry operations and symmetry elements of a molecule*

A symmetry or isometric operation that leaves distances and angles unchanged is an operation that brings a physical object from a given orientation to a new orientation that is equivalent to the former one. In the case of a molecule, the equilibrium configuration of the molecule is invariant under the symmetry operations associated with the symmetry elements of the molecule and therefore the molecule is brought to coincide with itself. There are two types of transformations: rotations of the three-dimensional space corresponding to the transformations of Euler r angles in the rotational space (direct operations) and other transformations such as inversion, reflections with respect to a plane, rotations followed by an inversion, rotations–reflections that reverse the direction of the mobile 3D reference frame (inverse operations).

The possible symmetry elements of a molecule that contribute to building a point group are rotation axes (operations termed as "direct"), inverse rotation axes, planes of reflection symmetry and an inversion center. There are five possible types of symmetry operations for a molecule (see Figure 1.1 and Table 1.1):

– identity operation E, equivalent to a rotation by 2π about C_n, ($C_z(\varphi = 2\pi)$) with $n = 1$ or an absence of operation ($C_z(\varphi = 0)$). The molecules remain unchanged under the action of E; E belongs to all the symmetry groups;

– a rotation by $2\pi/n$ about C_n, the rotation axis of order n; for a linear molecule, there are infinite possible rotations by angle φ about the internuclear axis z, the axis $C_z(\varphi)$ including the identity operation E; for $n = 2$ the molecule is an asymmetric top (H_2O); for $n = 3$, the molecule is a symmetric top (NH_3) if there is only one axis of symmetry of order 3; for $n = 4$ and because of the existence of four axes of symmetry of order 3, the CH_4 molecule is a spherical top. It is worth noting that it is a classification based on rigid rotators (see section 2.4) and on the symmetry about an axis. In general, if n is not a prime number, there is an integer k ($n = kp$), such that the p axes C_n^k are confounded with axis C_n. If there is an axis C_n with n even and a symmetry plane σ perpendicular to C_n, there is also a symmetry operation of inversion i;

– a rotation by $2\pi/n$ about the improper axis S_n, followed by the reflection operation in a plane perpendicular to the (rotation–reflection) axis; for a linear molecule, there is an infinity of improper rotations $S_z(\varphi)$ (rotation by an angle φ

about axis z followed by a reflection operation in a plane perpendicular to the axis at the center of the bond), including the reflection operation with respect to the plane *xy* (rotation by an angle 0 about the axis *z* and inversion S_2 with respect to the center of the bond); for a symmetric linear molecule, there is an infinity of rotations $C_t(\pi)$ by an angle π about axes *t* perpendicular to *z* and passing through the origin. If *n* is even, the axes C_{2n} are merged with axes S_n, ($S_n = C_{2n}$). If *n* is odd, the axes C_n are merged with axis S_n and there is a symmetry plane σ that is perpendicular to the axis S_n, ($S_n = C_n \otimes \sigma$). There is also the operation of inversion symmetry *i*. Generally, if *n* is odd and the axis is of type S_{2n}, then *i* exists;

– the symmetry planes σ_v, *v* stand for vertical (containing the highest-order rotation axis), σ_h, *h* stands for horizontal (perpendicular to the highest-order rotation axis) or σ_d, *d* stands for diagonal. For a linear symmetric molecule, there is an infinity of reflections $\sigma_{zt}(\sigma_v)$ with respect to *zt* planes containing the axis *z* and making an arbitrary angle with the *zx* plane; a molecule is invariant after the reversal of coordinates with respect to the symmetry plane σ;

– inversion *i* with respect to a center of symmetry of the molecule; for a linear symmetric molecule, S_2 corresponds to the inversion with respect to the center of the bond. Molecules that are invariant to this symmetry operation have an inversion center.

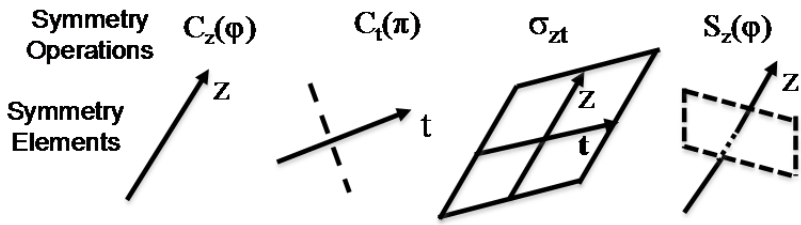

Figure 1.1. *Symmetry operations and symmetry elements of a molecule*

As an illustration, the symmetry elements of the NH_3 molecule are a third-order rotation axis (ternary axis: 2 rotation operations $C_z(2\pi/3)$ and $C_z(4\pi/3)$, denoted by C_3^1, and C_3^2 (see Figures 1.2(a) and 1.3), about the *Oz* axis passing through the nitrogen atom and three reflection symmetry planes $\sigma(0)$, $\sigma(2\pi/3)$ and $\sigma(4\pi/3)$, denoted by σ_v, σ_v' and σ_v'' (see Figures 1.2(b) and 1.3). If the identity operation E $(C_z(0))$ is added to these operations, the overlapping group of NH_3 and ND_3 molecules, denoted by C_{3v}, can be built (see Table 1.2). Generally, the *Oz* axis is placed along the highest-order rotational axis.

Symmetry operation	Herman–Mauguin	Schoenflies
Identity	1	C_1 or E
Rotation ($2\pi/n$)	n	C_n
Mirror	m	σ, C_s, S_1
Inversion	$\bar{1}$	i, C_i, S_2
Rotation-reflection	-	S_{2n}
Rotation-inversion	$\bar{n}$	-

Table 1.1. *Schoenflies and Hermann–Mauguin notations*

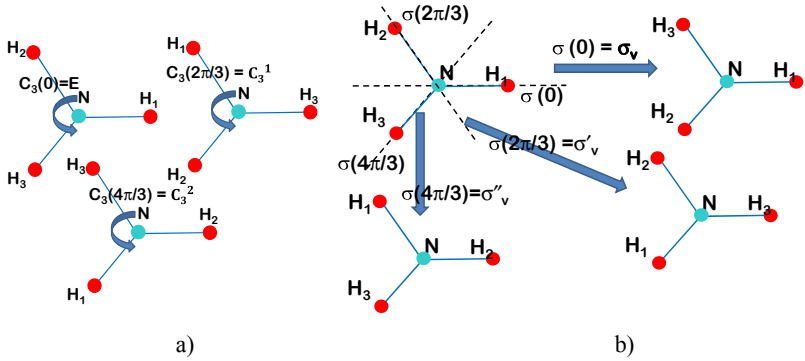

Figure 1.2. *Equivalent symmetry operations of plane rotation and reflection overlapping the equilibrium configurations of the NH_3 molecule. For a color version of this figure, see www.iste.co.uk/dahoo/infrared.zip*

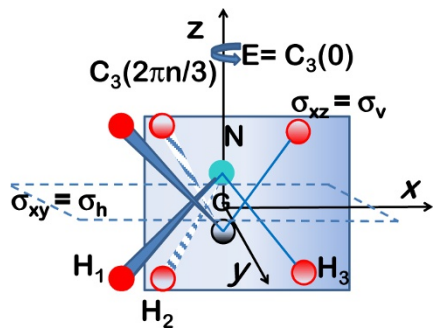

Figure 1.3. *Symmetry elements of the NH_3 molecule and its reversed equilibrium configuration. For a color version of this figure, see www.iste.co.uk/dahoo/infrared.zip*

C_{3v}	**E**	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3^1	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3^1	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3^1
σ_v''	σ_v''	σ_v	σ_v'	C_3^1	C_3^2	E

Table 1.2. *(Cayley) group C_{3v} multiplication table*

1.2.2. *Point symmetry group and laws of composition*

The set of symmetry operations of a molecule forms a point group (that leaves a point, invariant) in the mathematical sense [AMA 80a, BAR 88, BRA 72, BUN 98, CAM 88, COT 63, CRO 63, DEC 77, HAM 62, HER 45, LAN 75, MAR 83, MIX 72, TIN 03, WIG 59, WIL 55, WIL 80], and the symmetry elements can be regrouped into classes (symmetry operations that are equivalent: for NH_3, the two rotation operations $C_z(2\pi/3)$ and $C_z(4\pi/3)$, denoted by C_3^1 and C_3^2 (Figures 1.2(a) and 1.3), about the *Oz* axis passing through the nitrogen atom form a class, and the three planes of reflection symmetry $\sigma(0)$, $\sigma(2\pi/3)$ and $\sigma(4\pi/3)$ (Figures 1.2(b) and 1.3) form a second class.

The set of symmetry operations O_j constitutes a group if the following conditions are met:

– the product $O_k = O_iO_j$ of two operations of the set belongs to the set;

– the product is associative $O_i(O_jO_k) = (O_iO_j)O_k$;

– there is an operation E referred to as an identity such that $EO_i = O_iE = O_i$ (neutral element);

– each operation O_i can be put into correspondence with an operation O_i^{-1} known as the inverse of O_i, such that $O_iO_i^{-1} = O_i^{-1}O_i = E$.

If additionally $O_iO_j = O_jO_i$ (commutativity property), the group is referred to as "abelian".

The number of elements of a finite group is known as the "order of the group".

If two elements O and O' of a group G of order n are such that $O' = O_iOO_i^{-1}$ for any $O_i \in G$, the elements O and O' are conjugate. If O_i scans throughout group G,

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