1

Symmetry of Triatomic Molecules

With regard to the rotational and vibrational spectroscopy of a molecule, it is necessary to solve the Schrödinger eigenvalue equation to determine the quantum energy levels between which a transition leading to its spectral signature takes place. The study of these spectra makes it possible to determine its structure in rotational spectroscopy and the force fields responsible for the chemical bonds in vibrational spectroscopy. The symmetry of a molecule greatly influences the appearance of its absorption, emission or diffusion spectra. Based on the applications of group theory, it is possible to characterize the vibrational and rotational degrees of freedom of a triatomic molecule by the symmetry characteristics found in the structure corresponding to the molecule and to determine the transitions that are likely to be observed in an experiment, commonly called selection rules. Although the link between symmetry causes and symmetry effects are not directly obvious, as stated by Pierre Curie, it is easy to observe the consequences of the symmetry properties of molecules on the structure of the observed spectra, in absorption or emission spectroscopy or in Raman spectroscopy. Theoretical methods developed by J.M. Flaud and C. Camy-Peyret to establish the vibrational–rotational Hamiltonian of nonlinear triatomic molecules (H_2O, O_3, etc.) within the application of contact transformations of J.H. Van Vleck, based on J.K.G. Watson's work, show the need to consider the symmetries of the molecular structure to establish the correlation between the results of computations and observations.

1.1. Introduction

The vibrational and rotational spectroscopic study of triatomic molecules corresponds to the analysis of spectra resulting from absorption, emission or scattering processes of photons in the low-energy domain, ranging from microwaves to ultraviolet waves. In molecular physics, to determine the rovibrational energy levels of a molecule, the molecular Hamiltonian, established by E.B. Wilson and

J.B. Howard [WIL 36], reformulated by B.T. Darling and B.M. Dennison [DAR 40] and further simplified by J.K.G. Watson [WAT 68], is used in the context of J.H. Van Vleck's contact transformation [VAN 29, ALI 85] to determine the vibrational–rotational energy levels at different orders of approximation. The formalization of this method can be found in Chapter 2 of Volume 1 [DAH 17], with its application to diatomic molecules illustrated. This method uses unitary transformations that make it possible to group the Hamiltonian into interacting polyads and to obtain a block-like matrix form that is easier to diagonalize. From the method proposed by J.K.G. Watson [WAT 67a, WAT 67b, WAT 67c] to study isolated states theoretically, J.M. Flaud and C. Camy-Peyret [CAM 85] showed that the use of the symmetry properties of nonlinear triatomic molecules (H_2O, O_3, etc.) made it possible to construct the unitary transformations leading to the transformation of the initial Hamiltonian into interacting blocks that can be related to the experimental observations for the interacting vibrational levels.

While diatomic molecules are characterized by only one vibrational coordinate, it is necessary in the case of triatomic molecules to deal with more than one vibrational coordinate. Indeed, typically, a molecule with N atoms has 3N degrees of freedom. Three of these degrees of freedom are connected to the bulk translation of the molecule and thus of its center of mass and three (or two if the molecule is linear) to the bulk rotation of the molecule, these degrees of freedom are generally associated with low frequencies in the far infrared or the microwave range. The vibrational degrees of freedom that correspond to the deformation of the molecule can thus be written as the combination of 3N−6 harmonic vibrations (or 3N−5) each described by a normal coordinate Q_s. For N = 3, the number of normal coordinates is 4, if the molecule is linear; and 3, if it is nonlinear. The coordinates are generally characterized by their symmetries, which depend on the nature of the molecule, considering the properties of symmetry of the molecules; linear and nonlinear triatomic molecules which can be symmetrical or asymmetrical.

To take into account these symmetries, it is customary for using the results of group theory to highlight the consequences of symmetries in the spectroscopic study of molecules. We refer the reader to the Appendix of Chapter 1 of Volume 1 [DAH 17] which deals with diatomic molecules, with a review of the application of group theory to the study of molecules. Books can also be found in the literature that deal in more detail with group theory and its applications [WIL 80, LAN 75, CRO 63, HER 45, BUN 98].

In Chapter 2, we will discuss the symmetry of triatomic molecules from a group theory angle and we will start with the case of nonlinear molecules (O_3) by discussing the isotope $^{16}O^{16}O^{18}O$ (668), then $^{16}O^{18}O^{16}O$ (686) and $^{16}O^{16}O^{16}O$ (666), thus going from the least symmetrical to the most symmetrical, that is, from the simplest to the most elaborate group. We follow the approach that was developed by

J.M. Flaud and C. Camy-Peyret to review the symmetry properties of nonlinear triatomic molecules [FLA 81, CAM 85, FLA 90, FLA 13].

Then, we will discuss the case of linear molecules (CO_2) according to the same principle starting from the least symmetrical isotope $^{16}O^{12}C^{18}O$ (628) finishing with the most symmetrical, i.e. the isotope $^{16}O^{12}C^{16}O$ (626). It can be shown that the difference in the symmetry of these isotopes leads to different spectra in the infrared domain. We will specifically deal with the case of nitrous protoxide $^{14}N^{14}N^{16}O$ (446) because although the symmetries of isotopes 666 and 668 are different, carbon dioxide CO_2 is a symmetrical molecule whereas nitrous protoxide N_2O is not.

1.2. The symmetry group of the Hamiltonian of a triatomic molecule

The total Hamiltonian of a molecule (equation [1.6] in Volume 1 [DAH 17]) can be expressed in a frame based on the Eckart conditions [ECK 35], which makes it possible to strictly separate the translational degrees of freedom from the vibrational–rotational degrees of freedom; the second Eckart condition only allows an approximate separation of vibrational–rotational degrees of freedom. The Hamiltonian of order 0, without the coupling terms, thus simplified, can be expressed in the following form:

$$H_0 = T_{CM} + H_{eVR} + H_{SS} + H_{II} \qquad [1.1]$$

where T_{CM} is the kinetic energy of the center of mass (C.M.) of the nuclei; $H_{eVR} = H_e + H_V + H_R$ is the sum of the Hamiltonians relative to the movements of the electrons and the vibrational and rotational movements of the nuclei; H_{SS} (Spin–Spin interaction) refers to the interaction between electronic spins; and H_{II} (Spin–Spin interaction) refers to the interaction between nuclear spins. Note that the Born–Oppenheimer approximation or adiabatic approximation makes it possible to separate the movement of electrons from those of nuclei, that is, to study the movement of electrons for a fixed position of nuclei and the movement of nuclei in the mean field of electrons.

In the reference [BUN 98], the symmetry group G of the molecular Hamiltonian of a polyatomic molecule is expressed as the tensor product of a number of symmetry groups associated with the various constituents of the molecule, i.e. the electrons and the nuclei and their degrees of freedom. Group G has the following expression:

$$G = G_T \otimes K\left(spatial\right) \otimes S_n^{(e)} \otimes G^{CNP} \otimes \varepsilon \qquad [1.2]$$

where G_T is the spatial group associated with the translation of the center of mass; K(*spatial*) is the infinite group of rotations around an axis in a fixed frame passing through the center of mass; $S_n^{(e)}$ is the group associated with the permutations of electrons; G^{CNP} is the group associated with the permutations of the nuclei; and ε is the group associated with the inversion of the coordinates of all constituents (electrons and nuclei). This approach is general and concerns the total Hamiltonian of the polyatomic molecule and makes it possible to find the symmetry operations that leave the Hamiltonian invariant and that do not modify the energy of the molecule. Table 7.3 in reference [BUN 98] summarizes the characteristics of these symmetry operations. G_T and K(*spatial*) relate to the uniformity and isotropy of space; $S_n^{(e)}$ and G^{CNP} are connected to the indiscernibility of identical particles and are related to the nature of the electromagnetic force.

However, the use of an approximate Hamiltonian for calculating the wave functions and energy level solutions of the eigenvalue equation (given the approximation methods that are applied, such as the Van Vleck contact transformation in molecular physics) leads to the definition of symmetries based on symmetry groups as described in Chapter 1 of Volume 1 [DAH 17], to identify the symmetries of wave functions and energy levels. It is thus possible to identify by indices related to the symmetry properties of the molecule each vibrational–rotational state taking into account the spin properties and to determine the selection rules associated with the transitions leading to the spectra observed in the infrared or microwave domain. Note that these rules can be broken when the couplings are taken into account.

From the Hamiltonian of equation [1.1], the wave functions of a triatomic molecule can then be expressed as a product and the eigenenergies in the form of a sum such that:

$$|\Psi_0\rangle = |\Psi_{CM}\rangle \times |\Psi_e\rangle \times |\Psi_V\rangle \times |\Psi_R\rangle \times |Sm_S\rangle \times |\mathrm{Im}_I\rangle \qquad [1.3]$$

$$E_0 = E_{CM} + E_e + E_V + E_R + E_{SS} + E_{II} \qquad [1.4]$$

where $\Psi_{CM} = \langle R_{CM} | \Psi_{CM} \rangle$ is the wave function associated with the translational movement of the center of mass represented by a plane wave; $\Psi_e = \langle ..., r_e, ... | \Psi_e \rangle$ is the wave function associated with the movement of electrons which depends on the positions of the electrons; $\Psi_V = \langle Q | \Psi_V \rangle$ is the wave function associated with the vibrational motions of nuclei around their equilibrium position and which depends on the normal coordinates (3 for a nonlinear molecule and 4 for a linear molecule)

grouped in Q; $\Psi_R = \langle \theta, \varphi, \chi | JKM \rangle$ for a nonlinear triatomic molecule (in fact, $\Psi_R = \langle \theta, \varphi, \chi | JK_aK_c \rangle$ because we use the quantum numbers K_a and K_c as described in section 1.3) and $\Psi_R = \langle \theta, \varphi | JM \rangle$ for a linear triatomic molecule for the wave function associated with the overall rotational motion of the molecule around its center of mass; and $|Sm_S\rangle$ and $|Im_I\rangle$ are the electronic and nuclear spin wave functions, respectively. The wave functions associated with the different terms of H_0 (equation [1.1]) are transformed into irreducible representations (Chapter 1, Volume 1 [DAH 17]) of the groups that act in the different spaces of the different degrees of freedom (translation, vibration, rotation, spin) and which leave the Hamiltonian invariant. We can thus choose the good quantum numbers to identify the different vibrational–rotational energy levels. In the following, considerations of symmetry are discussed for the study of vibrational–rotational movements of a triatomic molecule in its fundamental electronic state.

To calculate the vibrational–rotational energy levels, we have to solve the Schrödinger eigenvalue equation that can be expressed in the following form:

$$H_{VR}|\Psi\rangle = (T_{VR} + V)|\Psi\rangle = E|\Psi\rangle \qquad [1.5]$$

where T_{VR} is the kinetic energy of vibration and rotation; V is the electronic potential, invariant by translation and rotation of all the nuclei and which only depends on internuclear distances; and E is the vibrational–rotational energy of the molecule in a reference frame denoted $(O,\vec{X},\vec{Y},\vec{Z})$, with uniform translation movement with respect to a fixed reference frame linked to the laboratory. The first Eckart's relation [ECK 35] involves fixing the origin of the mobile reference frame $(O,\vec{x},\vec{y},\vec{z})$ linked to the equilibrium configuration of the molecule at the center of mass G of the nuclei, such that:

$$\sum_{i=1}^{3} m_i \vec{\eta}_i = \vec{0} \qquad [1.6]$$

The second Eckart's condition [ECK 35] involves fixing the orientation of the molecule with respect to the instantaneous configuration of the nuclei, such that:

$$\sum_{i=1}^{3} m_i \vec{\eta}_i^{\,e} \wedge \vec{\eta}_i = \vec{0} \qquad [1.7]$$

In equations [1.6] and [1.7], $\vec{\eta}_i$ and $\vec{\eta}_i^{\,e}$ correspond to instantaneous and equilibrium positions of the nucleus i, with mass m_i.

1.3. Symmetry of the nonlinear triatomic molecule (O_3)

The study of the gas phase isotopically substituted molecule is similar to its unsubstituted counterpart (major isotopologues). In the case of triatomic molecules, the ozone molecule O_3 is completely symmetrical for the isotopologues $^{16}O^{16}O^{16}O$ (666) or $^{18}O^{18}O^{18}O$ (888). The same symmetry group can be used to study these molecules or others such as water vapor ($^{1}H^{16}O^{1}H$) or sulfur dioxide ($^{16}O^{32}S^{16}O$), which are similar to the isotopologues $^{16}O^{18}O^{16}O$ (686) or $^{18}O^{16}O^{18}O$ (868) of ozone. If we consider the isotopologue $^{16}O^{16}O^{18}O$ (668), we find symmetry properties different from isotopic varieties 666 or 686 and these molecular species belong to a different symmetry group.

By using the notations from reference [FLA 81], we can fix the axis Gx so that it passes through the central nucleus (Figure 1.1), the axis Gz being in the plane of the molecule.

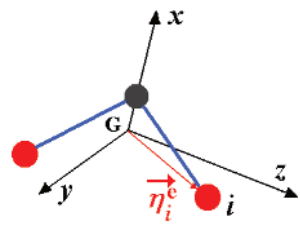

Figure 1.1. *Equilibrium configuration: moving axes of a nonlinear molecule. For a color version of this figure, see www.iste.co.uk/dahoo/infrared2.zip*

This choice is different from that which consists of fixing the axis Gz along the highest axis of rotation symmetry. In this case, the axis Gz coincides with a main axis of inertia of the ellipsoid of inertia of the molecule which does not coincide with the highest axis of symmetry.

By convention, in the case of nonlinear triatomic molecules (asymmetric tops), we choose the principal axes of inertia of the molecule as a system of axes which are generally denoted by Ga, Gb and Gc. According to the values of the moments of inertia I_a, I_b and I_c, the ellipsoid of inertia is either a flattened or elongated shape, which makes it possible to classify the molecule as being of either "oblate" in the form of disk or "prolate" like a rugby ball. Ga corresponds to the axis about which

the moment of inertia is the smallest and G*c* to the axis about which the moment of inertia is the greatest. There are six possibilities of matching the choice of the axes of the mobile frame to axes G*a*, G*b* and G*c*. Three of the representations correspond to direct orthonormal frame (r for "right") and three of the representations correspond to indirect orthonormal frame (l for "left") as indicated in Table 1.1.

	$\mathbf{I}^{\mathbf{r}}$	$\mathbf{II}^{\mathbf{r}}$	$\mathbf{III}^{\mathbf{r}}$	$\mathbf{I}^{\mathbf{l}}$	$\mathbf{II}^{\mathbf{l}}$	$\mathbf{III}^{\mathbf{l}}$
a	z	y	x	z	x	y
b	x	z	y	y	z	x
c	y	x	z	x	y	z

Table 1.1. *The six representations of orthonormal frames*

Typically, it is the I^r representation that is used.

When Van Vleck's contact transformation is applied to the H_{VR} Hamiltonian of a nonlinear triatomic molecule, we start from a zeroth-order Hamiltonian H^0 which is expressed as the sum of a vibrational Hamiltonian H_V^0 and a rotational Hamiltonian H_R^0 (Chapter 2, Volume 1 [DAH 17]) to determine eigenstates and vibrational–rotational energies. In this case, an eigenstate of H^0 is expressed in the form of a product of a vibrational eigenfunction and of a rotational eigenfunction such that:

$$\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3,J,K_a,K_c\right\rangle_0 = \left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0 \left|J,K_a,K_c\right\rangle_0 \qquad [1.8]$$

with

$$H_V^0 \left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0 = E_V^0\left(\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right)\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0 \qquad [1.9]$$

and

$$H_R^0 \left|J,K_a,K_c\right\rangle_0 = E_R^0\left(J,K_a,K_c\right)\left|J,K_a,K_c\right\rangle_0 \qquad [1.10]$$

In Chapter 2, we show that $\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0$ is the product of three Hermite functions (Chapter 2, equation [2.21]), eigenfunctions of three harmonic oscillators and that the zeroth-order vibration energy is given as follows:

$$E_V^0 = \omega_1\left(v_1 + \frac{1}{2}\right) + \omega_2\left(v_2 + \frac{1}{2}\right) + \omega_3\left(v_3 + \frac{1}{2}\right) \quad [1.11]$$

The rotational energy does not have a simple form because its computation occurs via the diagonalization of the zeroth-order rotational Hamiltonian in the basis of the eigenstates of the symmetric rigid rotator where K is the quantum number associated with the projection of the rotational angular momentum on the mobile axis Oz and M is the quantum number associated with the projection of the rotational angular momentum on the fixed axis OZ (Chapter 2).

Since the nonlinear triatomic molecule is an asymmetric top, the rotational levels are identified either by K_a eigenvalue of the angular momentum $\boldsymbol{J_a}$ in the case of a prolate symmetric top (rotational constant $A > B = C$), or by K_c eigenvalue of the angular momentum $\boldsymbol{J_c}$ in the case of an oblate symmetric top (rotational constant $A = B > C$). In the intermediate case, neither K_a nor K_c is a good quantum number, but an eigenstate is univocally defined by J, K_a and K_c, with:

$$0 \le K_a \le J \quad [1.12a]$$

$$0 \le K_c \le J \quad [1.12b]$$

$$K_a + K_c = J \quad \text{or} \quad J+1 \quad [1.12c]$$

such that the zeroth-order rotational state is denoted by $\left|J, K_a, K_c\right\rangle_0$. It should be noted that it is common to use an asymmetry parameter [RAY 32] defined by $\kappa = \frac{2B - A - C}{A - C}$ which varies from −1 to 1, to characterize the "oblate" or "prolate" nature of the asymmetric top molecule.

In the following, we discuss the symmetry properties of nonlinear triatomic molecules XYZ and XY_2 taking into account these properties in the infrared spectroscopic study of triatomic molecules, using the isotopologues of O_3 as examples. The method also applies to molecular species: H_2O, NO_2, SO_2, H_2S, etc.

1.3.1. *The nonlinear asymmetric molecule O_3 ($^{16}O^{16}O^{18}O$ (668))*

The nonlinear asymmetric molecule $^{16}O^{16}O^{18}O$ is of the type XYZ and belongs to the abelian symmetry group C_s. This symmetry group leaves the equilibrium configuration of the molecule invariant and transforms it into itself. This group consists of two symmetry operations which are the identity E ($C_2(2\pi)$) and the

reflection with respect to the plane of the molecule defined by the axes Gx and Gz denoted σ_{xz} (σ_h) (Figure 1.2). Table 1.2 shows the multiplication table of group C_s. The irreducible representations are of dimension 1 (abelian group), denoted by A′ and A″, and the normal vibrational coordinates are non-degenerate (Table 1.3).

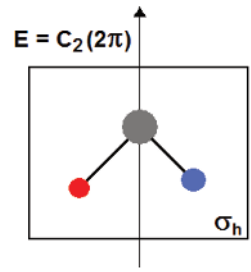

Figure 1.2. *Elements of symmetry of an XYZ-type nonlinear triatomic molecule. For a color version of this figure, see www.iste.co.uk/dahoo/infrared2.zip*

C_S	E	σ_{xz}
E	E	σ_{xz}
σ_{xz}	σ_{xz}	E

Table 1.2. *Multiplication table of group C_s*

	E	σ_{xz}	Polar vector	Axial vector	Normal coordinates
A′	1	−1	μ_x, μ_z	J_y	q_1, q_2, q_3
A″	1	1	μ_y	J_x, J_z	

Table 1.3. *Table of characters and symmetry properties of nonlinear molecules XYZ (C_s)*

1.3.2. *The nonlinear symmetric molecule O_3 ($^{16}O^{16}O^{16}O$ (666))*

The nonlinear symmetric molecule $^{16}O^{16}O^{16}O$ or $^{16}O^{18}O^{16}O$ is of type XY_2 and belongs to the C_{2v} symmetry group. It is an abelian symmetry group that leaves the equilibrium configuration of the molecule invariant and transforms it into itself. This group consists of four symmetry operations which are the identity E ($C_2(2\pi)$), the reflection with respect to the plane of the molecule defined by the axes Gx and Gz denoted σ_{xz} (σ_h), the reflection with respect to the plane xGy perpendicular to the

plane of the molecule denoted σ_{xy} (σ_v) and the rotation of an angle π about axis G*x* denoted C_2^x (C_2) (Figure 1.3).

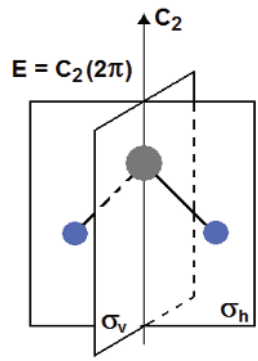

Figure 1.3. *Elements of symmetry of an XY_2-type nonlinear triatomic molecule*

C_{2v}	E	σ_{xy}	σ_{xz}	C_2^x
E	E	σ_{xy}	σ_{xz}	C_2^x
σ_{xy}	σ_{xy}	E	C_2^x	σ_{xz}
σ_{xz}	σ_{xz}	C_2^x	E	σ_{xy}
C_2^x	C_2^x	σ_{xz}	σ_{xy}	E

Table 1.4. *Multiplication table of group C_{2v}*

	E	σ_{xy}	σ_{xz}	C_2^x	Polar vector	Axial vector	Normal coordinates
A_1	1	1	1	1	μ_x		q_1, q_2
A_2	1	1	−1	−1		J_x	
B_1	1	−1	1	−1	μ_z	J_y	q_3
B_2	1	−1	−1	1	μ_y	J_z	

Table 1.5. *Table of characters and symmetry properties of nonlinear molecules XY_2 (C_{2v})*

Table 1.4 shows the multiplication table of group C_{2v}. The irreducible representations are of one dimension, denoted by A_1 and A_2, B_1 and B_2 and the vibrational normal coordinates are non-degenerate (Table 1.5).

1.3.3. *Symmetry of eigenstates of a nonlinear molecule*

Identifying the eigenstates of the zero-order Hamiltonian according to the two irreducible representations of group C_s or C_{2v} requires knowing the symmetry of a vibrational–rotational state, which is equal to the product of the symmetry of the vibrational state and that of the rotational state, such that:

$$\Gamma\left(\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3,J,K_a,K_c\right\rangle_0\right)=\Gamma\left(\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0\right)\times\Gamma\left(\left|J,K_a,K_c\right\rangle_0\right) \qquad [1.13]$$

The symmetry of the zeroth-order vibrational wave functions is determined by the parity of the Hermite polynomials. The wave function is an even function of the normal coordinate q if the quantum number v is even, and an odd function of the normal coordinate q if v is odd.

For the symmetry group C_s, all the normal coordinates being symmetric (Table 1.3), the symmetry of a vibrational state $\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0$ is of type A′ whatever the parity of the quantum numbers v_i. In the case of symmetry group C_{2v}, only the normal coordinate q_3 is of type B_1. This means that if v_3 is even, $\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0$ is of type A_1, and if v_3 is odd, $\left|\mathrm{v}_1,\mathrm{v}_2,\mathrm{v}_3\right\rangle_0$ is of type B_1.

With regard to the rotation, it is shown that the Hamiltonian of the rigid rotator (Chapter 2, equation [2.40]) is a sum of three terms each corresponding to the rotational kinetic energy with respect to an axis (Ox, Oy and Oz or Oa, Ob and Oc) passing through the center of mass of the equilibrium structure. This Hamiltonian operator is invariant with respect to the symmetry operations of group D_2 (or V), an abelian group corresponding to the three symmetry operations of rotation and of identity (Table 1.6). On the basis of the states of a symmetric top and in the absence of an external magnetic field, the eigenfunction $\left|J,k\right\rangle$ is expressed as a function of two quantum numbers J and k, associated with the operators $\mathbf{J}^2$ and $\boldsymbol{J}_z$ and its matrix elements connect the states k such that $\Delta k = 0, \pm 2$.

V(x,y,z)		**E**	$\boldsymbol{C_2^z}$	$\boldsymbol{C_2^x}$	$\boldsymbol{C_2^y}$
	V(a,b,c)	E	C_2^a	C_2^b	C_2^c
A	A	1	1	1	1
$\mathbf{B_x}$	B_a	1	1	−1	−1
$\mathbf{B_y}$	B_b	1	−1	1	−1
$\mathbf{B_z}$	B_c	1	−1	−1	1

Table 1.6. *Table of characters of the groups V(x,y,z) and V(a,b,c)*

To study the symmetry of the rotational states $\left|J, K_a, K_c\right\rangle_0$, it is necessary to introduce a set of symmetrical states on the basis of the states of the symmetric top, by constructing a symmetrical basis (also called the Wang basis [WAN 29]), such that:

$$\left|J, K, \gamma\right\rangle = \frac{1}{\sqrt{2}}\left(\left|J, k\right\rangle + \gamma\left|J, -k\right\rangle\right) \qquad [1.14a]$$

$$\left|J, 0, +\right\rangle = \left|J, 0\right\rangle \qquad [1.14b]$$

with $K = |k|$ and $\gamma = \pm$.

Depending on the parity of K and the sign of γ, the functions can be grouped together (Table 1.7) so as to generate four subspaces E^+, E^-, O^+ and O^-, E for even K and O for odd K. For K = 2p, even, E^+ is of dimension p+1, and E^- is of dimension p. For K = 2p+1, odd, O^+ and O^- are of dimension p.

Fixed space J	Dimension	K	Base
E^+(p)	p+1	Even	$\{\|2p,+\rangle, \|2p-2,+\rangle, \ldots \|0,+\rangle\}$
E^-(p)	p	Even	$\{\|2p,-\rangle, \|2p-2,-\rangle, \ldots \|2,-\rangle\}$
O^+(p)	p	Odd	$\{\|2p-1,+\rangle, \ldots \|1,+\rangle\}$
O^-(p)	p	Odd	$\{\|2p-1,-\rangle, \ldots \|1,-\rangle\}$

Table 1.7. *Table showing the characteristics of subspaces E^+, E^-, O^+ and O^-*

Considering the invariance of the rotational Hamiltonian with respect to the symmetry group $V(a,b,c)$ of the ellipsoid of inertia of the molecule, the types of symmetry of the states $\left|J, K, \gamma\right\rangle$ can be studied with respect to this group (Table 1.8) starting from the equivalence between the symmetry elements of group $V(x,y,z)$ and the rotational operators, taking into account the choice of the representation I^r (x=b, y=c, z=a) (Table 1.1).

	J even	J odd
E^+(k even)	A	B_a
E^-(k even)	B_a	A
O^+(k odd)	B_b	B_c
O^-(k odd)	B_c	B_b

Table 1.8. *Type of symmetry of functions with respect to the group V(a,b,c)*

Moreover, since the function $|J, K_a, K_c\rangle_0$ must be characterized by the same type of symmetry as the two functions $|J, k\rangle_{\kappa=+1}$ and $|J, k\rangle_{\kappa=-1}$, as the limiting cases of the asymmetric top when A = B (oblate asymmetric top) and when B = C (prolate asymmetric top), it can be shown from the table of characters of the group $V(a,b,c)$ (Table 1.6) that the type of symmetry of the functions $|J, K_a, K_c\rangle_0$ depends on the parity of the quantum numbers K_a and K_c as presented in Table 1.9.

K_a	K_c	V(a,b,c) Type	V(x,y,z) Type
e	e	A	A
e	o	B_a	B_z
o	o	B_b	B_x
o	e	B_c	B_y

Table 1.9. *Type of symmetry of rotational levels with respect to groups V(a,b,c) and V(x,y,z)*

Choosing the representation I^r makes it possible to establish an isomorphism between $V(a,b,c)$ and $V(x,y,z)$ on the one hand and as $V(x,y,z)$ and group C_{2v} are also isomorphic, the types of symmetry of the rotational levels can be determined from the correspondence between the irreducible representations with respect to groups C_{2v} and C_s which is a subgroup of C_{2v} as shown in Table 1.10.

K_a	K_c	V(a,b,c) Type	C_{2V} Type	C_S Type
e	e	A	A_1	A′
e	o	B_a	A_2	A″
o	o	B_b	B_1	A′
o	e	B_c	B_2	A″

Table 1.10. *Equivalence between irreducible representations of groups V(a,b,c), C_{2v} and C_s*

Finally, the symmetry type of the vibration–rotation eigenstates (equation 1.15) can be determined for the two types of molecules, XY_2 and XYZ, as given in Table 1.11 from the symmetries of the vibrational and rotational states. Note that it is easier to calculate the matrix elements of the vibration–rotation Hamiltonian operators at the different perturbation orders using the Wang symmetric basis. In this

case, the wave functions $\left|v_1,v_2,v_3,J,K_a,K_c\right\rangle_0 = \left|v_1,v_2,v_3\right\rangle_0 \left|J,K_a,K_c\right\rangle_0$ are developed on this basis respecting the types of symmetries such that:

$$\left|v_1,v_2,v_3,J,K_a,K_c\right\rangle_\Gamma = \sum_{\mathrm{v}}\sum_{K} C_K^{\mathrm{v}} \left|\mathrm{v}\right\rangle_{\Gamma_{\mathrm{v}}} \left|J,K,\gamma\right\rangle_{\Gamma_{\mathrm{r}}} \qquad [1.15]$$

with $\Gamma_{\mathrm{V}} = \Gamma(\mathrm{v})$, $\Gamma_{\mathrm{r}} = \Gamma\left(\left|\mathrm{J,K},\gamma\right\rangle\right)$ and $\Gamma = \Gamma_{\mathrm{V}} \times \Gamma_{\mathrm{r}}$.

The symmetry types of the symmetrized functions $\left|J,K,\gamma\right\rangle$ belonging to the different subspaces E^+, E^-, O^+ and O^- are given in Tables 1.12 and 1.13 for XY_2- and XYZ-type molecules, respectively. With this basis, the matrix of the Hamiltonian operator splits into four submatrices corresponding to the four types of symmetry.

K_a	K_c	XYZ (C_S) ($\forall v_1,v_2,v_3$) Type	v_3	XY_2 (C_{2V}) ($\forall v_1,v_2$) Type
e	E	A′	e	A_1
o	e	A′	o	A_1
o	o	A″	e	A_2
e	o	A″	o	A_2
o	e	A′	e	B_1
e	e	A′	o	B_1
e	o	A″	e	B_2
o	o	A″	o	B_2

Table 1.11. *Symmetry types of the vibration–rotation states for a molecule of type XYZ and of type XY_2, respectively with respect to groups C_s and C_{2v}*

	J even Type of symmetry	J odd Type of symmetry
E^+	A_1	B_2
E^-	B_2	A_1
O^+	A_2	B_1
O^-	B_1	A_2

Table 1.12. *Types of symmetry of the subspaces E^+, E^-, O^+ and O^- of group C_{2v}*

	J even Type of symmetry	J odd Type of symmetry
$\mathbf{E}^+$	A′	A″
$\mathbf{E}^-$	A″	A′
$\mathbf{O}^+$	A″	A′
$\mathbf{O}^-$	A′	A″

Table 1.13. *Types of symmetry of the subspaces E^+, E^-, O^+ and O^- of group C_s*

Note that in the case of XY_2 molecules, it is necessary to take into account the symmetry in the exchanges of identical nuclei.

1.4. Symmetry of the linear triatomic molecule (CO_2)

Carbon dioxide (CO_2) is a linear triatomic molecule characterized by four normal vibrations. If we are interested in the isotopologues of CO_2, we can separate the symmetric isotopes such as $^{16}O^{12}C^{16}O$ (626) and asymmetric varieties such as $^{16}O^{12}C^{18}O$ (628).

To identify the symmetry elements of the linear CO_2, the axes system used to identify the equilibrium configuration of the molecule is oriented differently from that used for the nonlinear triatomic molecules. The axis Gz linked to the molecule coincides with the axis of infinite order of rotation symmetry (the highest axis of rotation symmetry) which leaves the equilibrium configuration of the molecule invariant and which is parallel to the internuclear axis as for a diatomic molecule (Chapter 1, Volume 1 [DAH 17]).

This choice is different from that which consists of fixing the axis Gz along an axis of inertia of the molecule as for a nonlinear molecule which does not coincide with an axis of rotation symmetry. In this case, the axis Gz being aligned along the internuclear axis, the other two axes perpendicular to Gz and also between them have any orientation (Figure 1.2). The movement of the nuclei is split into a rotational movement of the reference configuration and a vibrational motion. The mobile frame $(O,\vec{x},\vec{y},\vec{z})$ whose origin coincides with the center of mass (Figure 1.4, first condition of Eckart or Eckart-Sayvetz) moves with the molecule with respect to a fixed frame (laboratory frame $(O,\vec{X},\vec{Y},\vec{Z})$), its rotation being defined by two Euler angles θ and φ. In this frame, the vibrations are defined by the instantaneous positions of the nuclei with respect to their equilibrium positions. The axis of the reference configuration coincides with the axis of the instantaneous configuration

and the vibration is described by four normal coordinates Q_i (i = 1, 2, 3, 4), two of which are degenerate.

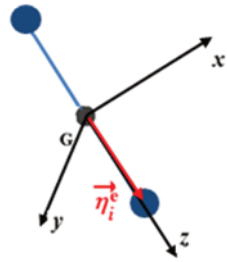

Figure 1.4. *Equilibrium configuration: mobile axes of a linear molecule. For a color version of this figure, see www.iste.co.uk/dahoo/infrared2.zip*

This choice is different from that which involves fixing the axis Gz along the highest-order axis of rotation symmetry.

When Van Vleck's contact transformation is applied to the Hamiltonian H_{VR} of a linear triatomic molecule, we start, as for the nonlinear triatomic molecule, from a zeroth-order Hamiltonian H^0 expressed as the sum of a vibrational Hamiltonian H_V^0 and a rotational Hamiltonian H_R^0 (Chapter 2, Volume 1 [DAH 17]) to determine the eigenstates and vibration–rotation energies. In this case, an eigenstate of H^0 is expressed as a product of a vibrational eigenfunction and a rotational eigenfunction, such that:

$$\left|\mathrm{v}_1,\mathrm{v}_{21},\mathrm{v}_{22},\mathrm{v}_3,J,M\right\rangle_0 = \left|\mathrm{v}_1,\mathrm{v}_{21},\mathrm{v}_{22},\mathrm{v}_3\right\rangle_0 \left|J,M\right\rangle_0 \qquad [1.16]$$

with

$$H_V^0 \left|\mathrm{v}_1,\mathrm{v}_{21},\mathrm{v}_{22},,\mathrm{v}_3\right\rangle_0 = E_V^0\left(\mathrm{v}_1,\mathrm{v}_{21},\mathrm{v}_{22},\mathrm{v}_3\right)\left|\mathrm{v}_1,\mathrm{v}_{21},\mathrm{v}_{22},\mathrm{v}_3\right\rangle_0 \qquad [1.17]$$

and

$$H_R^0 \left|J,M\right\rangle_0 = E_R^0\left(J,M\right)\left|J,M\right\rangle_0 \qquad [1.18]$$

In Chapter 2 (equation [2.22]), we show that $\left|\mathrm{v}_1,\mathrm{v}_{21},\mathrm{v}_{22},\mathrm{v}_3\right\rangle_0$ is the product of two Hermite functions, eigenfunctions of two one-dimensional harmonic oscillators

and a Laguerre function, eigenfunction of a two-dimensional harmonic oscillator (doubly degenerate). To identify the doubly degenerate vibrational levels, we use two other quantum numbers v_2 and ℓ_2, where ℓ_2 is associated with the quantum number of internal rotation ($|\ell_2| = v_2, v_2-2, \ldots 0$ or 1) restricted to the doubly degenerate space. At the zeroth-order, a vibrational state is thus denoted by $|v_1, v_2, \ell_2, v_3\rangle_0$, and the zeroth-order vibrational energy is expressed by (Chapter 2, equation [2.24]):

$$E_V^0(v_1, v_2, \ell_2, v_3) = \omega_1\left(v_1 + \frac{1}{2}\right) + \omega_2(v_2 + 1) + \omega_3\left(v_3 + \frac{1}{2}\right) + g_{22}^{v}\ell_2^2 \quad [1.19]$$

In this expression, g_{22}^{v} is the degree of degeneracy of the energy level $E(v_2, \ell_2)$ such that $g_{22}^{v} = \dfrac{(v_2+1)(v_2+2)}{2}$.

The rotational energy of the linear triatomic molecule depends on two quantum numbers associated with the two Euler angles θ and φ as for a diatomic molecule (Chapter 2, Volume 1 [DAH 17]). The rotational eigenstates are characterized by two quantum numbers (J, M). In the absence of a magnetic field, the rotational energy has the following expression:

$$E_J^0(J, M) = B^e J(J+1) \quad [1.20]$$

where $B^e = \hbar^2 / 2I^e$ is the rotational constant of the rigid molecule. An eigenstate is denoted by $|J, M\rangle_0$, with $0 \le |M| \le J$.

Next, we discuss the symmetry properties of XYZ and XY_2 linear triatomic molecules and their consideration in the infrared spectroscopic study of linear triatomic molecules.

1.4.1. *The linear asymmetric molecule CO_2 ($^{16}O^{12}C^{18}O$ (628))*

The linear asymmetric molecule 628 is of type XYZ. The symmetry properties of the molecule are determined from the overlapping group of the nuclei equilibrium configuration [LAN 75, WIL 80, AMA 80, CAM 85]. From the frame tied to the equilibrium configuration of the molecule and moving with it, the overlapping group

is established by identifying the changes in this frame which superimposes the equilibrium configuration itself.

For XYZ-type molecules, the covering group $C_{\infty v}$ (Table 1.14) consists of the following symmetry operations:

– infinity of rotations $C_z(\varphi)$ of an angle φ about axis z including the identity operation I;

– infinity of reflections σ_{zt} with respect to zt planes containing z and forming any angle with plane zx.

The symmetry elements of XYZ molecules are, respectively, the rotational axis of the first species z and the symmetry planes zt (Figure 1.5).

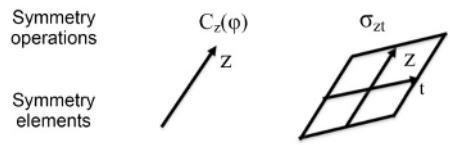

Figure 1.5. *Operations and elements of symmetry of a linear triatomic molecule of type XYZ*

The linear asymmetric molecule 628, which is of type XYZ, therefore belongs to the $C_{\infty v}$ symmetry group (Table 1.14). Note that in the general case, the group C_∞ is the rotational group of a cone.

$C_{\infty V}$	I	$2C_\infty(\varphi)$	$^\infty\sigma_V$	
Σ^+	1	1	1	μ_Z, T_Z, q, Ψ
Σ^-	1	1	−1	J_Z
Π	2	2cosφ	0	(μ_X, μ_Y) (T_X, T_Y) (J_X, J_Y)
Δ	2	2cosφ	0	
Φ	2	2cosφ	0	

Table 1.14. *Symmetry group $C_{\infty v}$: table of characters*

Defining the symmetry types of group $C_{\infty v}$ reflects the behavior of physical quantities and other molecular properties with respect to the symmetry operations of this group. Thus, the symbols Σ, Π, Δ, etc. reflect the behavior with respect to the rotation $C_z(\varphi)$; the irreducible representations amount to two for those of one dimension with cylindrical symmetry (Σ) and to an infinite number for the others

that are two-dimensional ($\Pi,\Delta,\Phi,\ldots$); the sign + or – affecting the symbol Σ (electronic distribution with the symmetry of revolution around z or invariant states in a symmetry of revolution around z) reflects the symmetrical or antisymmetric character with respect to reflection σ_{zt}. Consequently, the irreducible representations of the overlapping group $C_{\infty v}$ of the linear triatomic XYZ molecule are denoted by Σ^+, Σ^-, Π, Δ, Φ, Γ.... and serve to identify the symmetry properties of the rovibronic states.

1.4.2. *The linear symmetric molecule CO_2 ($^{16}O^{12}C^{16}O$ (626))*

The linear symmetric molecule $^{16}O^{12}C^{16}O$ (626) is a centro-symmetric XY_2-type linear triatomic molecule with no permanent dipole moment. The configuration of linear symmetric molecules (626), of type XY_2, with two indiscernible nuclei (^{16}O,^{16}O) corresponds to the overlapping group $D_{\infty h}$ (Table 1.15), which includes the following symmetry operations (Figure 1.4):

– infinity of rotations $C_z(\varphi)$ of an angle φ about axis z including the identity operation I;

– infinity of improper rotations $S_z(\varphi)$ (rotation of angle φ about axis z and inversion with regard to the center of the bond), including the reflection operation with respect to the xy plane (rotation of angle 0 about axis z and inversion with regard to the center of the bond);

– infinity of rotations $C_t(\pi)$ of an angle π about axes t perpendicular to z and passing through the origin;

– infinity of reflections σ_{zt} with respect to planes zt containing axis z and forming any angle with plane zx.

The elements of symmetry of the linear symmetric molecule 626, type XY_2, are respectively the axis of rotation of the first species z (which includes the identity), axes of rotation, planes of symmetry zt and the axis of rotation of the second species z (which includes inversion) (Figure 1.4). Note that in the general case, the group $D_{\infty h}$ is the rotation group of a cylinder.

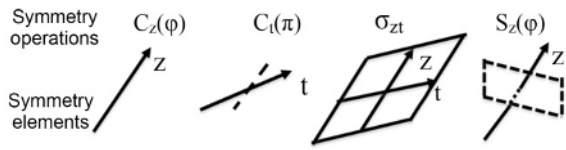

Figure 1.6. *Operations and elements of symmetry of a linear triatomic molecule of type XY_2*

$D_{\infty h}$	I	$2C_\infty(\varphi)$	$^\infty\sigma_V$	i	$2S_\infty(\varphi)$	$^\infty C_2$	
Σ_g^+	1	1	1	1	1	1	q, Ψ
Σ_u^+	1	1	1	−1	−1	−1	μ_Z, T_z
Σ_g^-	1	1	−1	1	1	−1	J_Z
Σ_u^-	1	1	−1	−1	−1	1	
Π_g	2	2cosφ	0	2	−2cosφ	0	(μ_X, μ_Y) (T_X, T_Y)
Π_u	2	2cosφ	0	−2	2cosφ	0	(J_X, J_Y)
Δ_g	2	2cosφ	0	2	2cosφ	0	
Δ_u	2	2cosφ	0	−2	−2cosφ	0	

Table 1.15. *Symmetry group $D_{\infty h}$: table of characters*

As for the group $C_{\infty v}$, defining the types of symmetry of group $D_{\infty h}$ reflects the behavior of physical quantities and other molecular properties with respect to symmetry operations. Thus, we find the symbols Σ, Π, Δ… which reflect the behavior with respect to the rotation $C_z(\varphi)$; the irreducible representations amount to 2 for those of one-dimension with complete cylindrical symmetry (Σ) and to an infinite number for the others that are two-dimensional (Π, Δ, Φ,…); similarly, the sign + or − affecting the symbol Σ (electronic distribution with the symmetry of revolution around z or invariant states in a symmetry of revolution around z) reflects the symmetrical or antisymmetric character with respect to reflection σ_{zt}.

The symmetry operations of group $D_{\infty h}$ are twice those of group $C_{\infty v}$ as a result of the existence of the inversion operation. For group $D_{\infty h}$, the index g (gerade or even) or u (ungerade or odd) reflects the symmetrical or antisymmetric character with respect to the inversion. As a result, the irreducible representations of the covering group ($D_{\infty h}$) of the XY_2 linear triatomic molecule are denoted by Σ_g^+, Σ_u^+, Σ_g^-, Σ_u^-, Π_g, Π_u, Δ_g, Δ_u, Φ_g, Φ_u, Γ_g, Γ_u.... and these symbols are used to identify the symmetry properties of the rovibronic states.

In the case of XY_2 molecules, it is necessary to take into account the symmetry in the exchanges of identical nuclei.

1.5. Selection rules

To discuss the selection rules, we refer to the elements presented in Chapter 1 of Volume 1 [DAH 17]. The possible transitions between the quantum states at the origin of the spectra observed depend on the symmetry of these states. A transition between two quantum states is possible if at least one of the integrals of the type:

$$R_{mn} = \left\langle \Psi_{eVR}^{m} \middle| R \middle| \Psi_{eVR}^{n} \right\rangle = \int \Psi_{e}^{m*} \Psi_{V}^{m*} \Psi_{R}^{m*} R \Psi_{e}^{n} \Psi_{V}^{n} \Psi_{R}^{n} d\tau \qquad [1.21]$$

is different from zero and therefore symmetrical with respect to the symmetry operations that leave the molecule invariant. In this expression, R is the operator that is responsible for the radiation–matter interaction and $|\Psi_m\rangle = \left|\Psi_{eVR}^{m}\right\rangle$ represents a vibration–rotation state when the molecule is in a given electronic state. The representation $\Gamma(|\Psi_m\rangle) \otimes \Gamma(|\Psi_n\rangle) \otimes \Gamma(R)$ must contain the unit representation so that the integral of equation [1.21] is non-zero. This means that the symmetry of the product of the two states between which the transition occurs must be of the same type of symmetry as that of the operator R.

During the exchange of isotopic nuclei of the same type, the XY_2-type molecules (nonlinear and linear) have a symmetry which also influences the shape of the spectra observed in emission (respectively, absorption) and in Raman scattering. To account for the spin of electrons and nuclei, we start from the total wave function (equation [1.3]) which is expressed by including the spin variables of the electrons in the electronic wave function, so that only the effect of the exchange of the identical nuclei is taken into account to determine the symmetry of the total wave function. The wave function is written as follows: $|\Psi_t\rangle = (|\Psi_e\rangle \times |Sm_S\rangle) \times |\Psi_{VR}\rangle \times |Im_I\rangle$. For the electronic part, the spin effect imparts symmetry to the electronic wave functions of the space variables which may be symmetrical or asymmetric. The integrand of equation [1.21] is multiplied by the integral on the quantum spin variables such that: $\left\langle I^m m_I^m \middle| I^n m_I^n \right\rangle$.

In infrared spectroscopy, the operator R is one of the components (μ_x, μ_y, μ_z) of the electric dipole moment in the case of absorption or emission of photons (absorption or emission spectroscopy). In elastic (Rayleigh, Mie) or inelastic (Raman, Brillouin) scattering, R is one of the operators related to the elements α_{xx}, α_{yy}, α_{zz}, α_{xy}, α_{yz}, α_{xz} of the molecular polarizability tensor.

1.5.1. *Symmetry of the eigenstates of a triatomic molecule taking into account the nuclei spins*

Only the spectra of XY_2 molecules have structures directly related to the exchange of the identical nuclei in the molecule. As already discussed in Chapter 1 of Volume 1 [DAH 17] for diatomic homonuclear molecules, this effect can be

determined using the properties of the permutation operator of two particles. The total wave function may be invariant or may change sign in a permutation operation of indiscernible particles. This corresponds to the two eigenvalues −1 and +1 of the permutation operator of two particles, which leads, depending on whether the wave function is symmetrical (+1) or antisymmetric (−1) in the permutation operation, to classify the wave functions into "*s*" states and "*a*" states.

The effect of the operator R in equation [1.21] leading to observable spectra in emission or absorption spectroscopy (electric dipole moment, electric quadrupole moment, magnetic dipole moment), in Raman scattering spectroscopy (polarizability) or in collision spectroscopy (collision operator) is computable from the transition moment $\langle \Psi_t' | R | \Psi_t'' \rangle$. It is shown that since the operator R is invariant in an exchange operation of two identical nuclei, the product $\langle \Psi_t' | \Psi_t'' \rangle$ must also be invariant, which implies that both $|\Psi_t'\rangle$ and $|\Psi_t''\rangle$ are symmetric or asymmetric. Therefore, the states can be grouped into two classes, since a molecular system is either in a symmetrical state or in an asymmetrical state. In the case of mass number M containing M spin 1/2 particles, exchanging two nuclei is equivalent to exchanging spin 1/2 particles M times. The wave function $|\Psi_t\rangle$ changes sign at each exchange of two particles, so that $|\Psi_t\rangle$ is symmetrical or antisymmetric depending on whether M is even or odd. The nuclear spin wave function which is quantum in nature depends on the mass number M of the nucleus (M even: integer spin obeying the Bose–Einstein statistic; M odd: half-integer spin obeying the Fermi–Dirac statistic) (Table 1.6, Chapter 1, Volume 1 [DAH 17]). These different properties are responsible for the structures present in the IR and Raman spectra of XY_2 triatomic molecules. The nuclear spin wave function can be put in the form of a product: $|\Psi_I\rangle = \left|\Psi_i^{(1)}\right\rangle \times \left|\Psi_j^{(2)}\right\rangle$, an expression that is interpreted with the nucleus numbered 1 in spin state i and the nucleus numbered 2 in spin state j. The states i and j are characterized by the value of the quantum number I which can take $2I+1$ values $(-I, -(I-1), \ldots\ldots, I-1, I)$, where I denotes the spin of the nucleus.

To determine the symmetry of an electronic or vibrational wave function, we must know how the electronic position coordinates and the vibrational normal coordinates are transformed in a symmetry operation [LAN 75, WIL 80, AMA 80, CAM 85]. In this case, the symmetry operation is defined as a change in the reference axes system *xyz* accompanied by a permutation of indices numbering identical nuclei. The reference system is rotated relative to the equilibrium or instantaneous configuration of the nuclei.

In general, it can be shown that for a nucleus spin I, there are $(2I+1)(I+1)$ symmetrical functions and $(2I+1)(I)$ antisymmetric functions. Symmetrical states are called *ortho* states and antisymmetric states are called *para* states. *Ortho* states are always more numerous than *para* states. When $I = 0$, there is no *para* state. A state can also be characterized from the composition of the spins of each nucleus, that is, $|I_1 - I_2| \le T \le |I_1 + I_2|$; $(T = 0, 1, ...2I)$ and the projection of T on the internuclear axis $-T \le M_T \le +T$; $\Delta M_T = +1$. We show that the *ortho* states correspond to the even T states and the *para* states correspond to the odd T states, valid independently of the statistic: Bose–Einstein or Fermi–Dirac.

When considering the total wave function $|\Psi_t\rangle = |\Psi_{eVR}\rangle|\Psi_I\rangle$, the product must be symmetrical if the nuclei obey the Bose–Einstein statistic and must be antisymmetric if the nuclei obey the Fermi–Dirac statistic. As a result, the relative statistical weight of type "*s*" $|\Psi_{eVR}\rangle_s$ states and type "*a*" $|\Psi_{eVR}\rangle_a$ states depends on the type of statistics. We have $\dfrac{|\Psi_{eVR}\rangle_s}{|\Psi_{eVR}\rangle_a} = \dfrac{I+1}{I}$ if the nuclei obey the Bose–Einstein statistic and $\dfrac{|\Psi_{eVR}\rangle_s}{|\Psi_{eVR}\rangle_a} = \dfrac{I}{I+1}$ if the nuclei obey the Fermi–Dirac statistic. If $I = 0$, only $|\Psi_{eVR}\rangle_s$ states are present (half number of levels are absent, there are no *para* states).

The spins are half-integers for nuclei with odd mass numbers and integers for nuclei with even mass numbers, that is, ½ for H, 0 for O and 1 for D and N, for example. In the case of linear or nonlinear XY_2 molecules, the total wave function must be symmetrical or antisymmetric in the exchange of the nuclei, that is, the exchange of spins. Examples of linear molecules are CO_2, LiH_2, BeH_2 and examples of nonlinear molecules are O_3, H_2O, D_2O, H_2S, H_2Se, NO_2 or SO_2. With regard to the linear triatomic molecule CO_2 whose fundamental electronic state is completely symmetrical of type Σ_g^+, since the spin of the oxygen nucleus O is equal to 0, only the levels of even J are filled. This same structure is present in the spectra of O_3, NO_2 or SO_2 molecules when oxygen atoms are identical. For the nonlinear molecule H_2O, with the exchange of nuclei obeying the Fermi–Dirac statistic, there is a ratio of $I/(I+1)$ between the transition intensities between symmetrical vibration–rotation states and the transition intensities between the antisymmetric vibration–rotation states. In the case of D_2O, the ratio is $(I+1)/I$.