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Generalities on Diatomic Molecules

A diatomic molecule is the simplest possible assembly based on a system of atoms that lead to molecules, whether homonuclear or heteronuclear. Its spectral signature is the result of the interaction of an electromagnetic radiation with the electrons, given the movement of its charged constituents, nuclei and electrons. This interaction is modeled by an operator, the n-polar moment, which leads to a transition between the diatomic molecule’s energy states, the eigenfunctions of the Hamiltonian, its energy operator built on the classical (electronic, vibration and rotation) and quantum (electronic and nuclear spin) degrees of freedom. The resolution of the Schrödinger eigenvalues equation of the molecular system is based on the Born–Oppenheimer (BO) approximation, which allows the electrons’ fast movement to be decoupled from that of the nuclei, which is much slower, and to separately process its electronic and vibration–rotation degrees of freedom in spectroscopy. The characteristics of the electronic, vibrational and rotational spectra depend on the molecule’s symmetries and its electronic and nuclear spin properties. We can use group theory for predicting the absorption spectra profiles and the transition rules expected in infrared or Raman spectroscopy. Thus, molecular species are divided into para and ortho varieties for the H_2 molecule, for instance. In the Raman rotational spectrum, H_2 presents an intensity alternation which is different to that of N_2 as a function of the rotational quantum number, whereas for O_2, one line out of two is absent in the spectrum.

1.1. Generalities on detecting diatomic molecules

1.1.1. *Radiation–matter interaction for detection*

The presence of a molecule may be revealed by probing a given medium with an electromagnetic radiation favorable for it to be observed in the frequency range corresponding to radio waves, microwaves, millimetric waves, Térahertz radiation, infrared radiations (far, mid, near), visible light, ultraviolet radiations or X-rays. Different techniques have been developed for studying molecules according to the type of interaction (linear, nonlinear, emission, absorption, diffusion, etc.) and the spectral region.

As a general rule, the interaction of an electromagnetic radiation with a molecule (Figure 1.1), whether diatomic or polyatomic, results in physical–chemical processes such as the absorption or emission of photons (spectroscopy of absorption or emission), elastic diffusion (Rayleigh, Mie) or inelastic diffusion (Raman, Brillouin), phenomena of dissociation, ionization or a combination of these processes. These processes involve transitions between discrete energy levels and a continuum of levels following the interaction between the multipolar moments of the molecule and the electrical field of the radiation. The interaction between an electromagnetic wave and matter was discussed more thoroughly in a previous publication (Chapter 3 [DAH 16]).

To each state of a molecule, the quantum mechanics theory associates a wave function that depends on the position coordinates and the spins of the two nuclei and electrons comprising the molecule. In order to determine the molecule's quantum state, one must solve the Schrödinger eigenvalues equation of the molecular system:

$$H\left|\Psi\right\rangle = E\left|\Psi\right\rangle, \qquad [1.1]$$

where H is the energy operator, corresponding to the Hamiltonian of the molecular system and $\left|\Psi\right\rangle$ is the wave function of the system expressed in Dirac's notation.

In the case of an electric dipolar transition between the states $\left|\Psi_i\right\rangle$ and $\left|\Psi_f\right\rangle$, the probability of a radiative transition is given by Einstein's spontaneous emission coefficient:

$$A_{if} = \tau^{-1} = \frac{64\pi^4}{h}\frac{g_i}{g_f}\nu_{if}^3\left|R_{if}\right|^2 \qquad [1.2]$$

where τ is the radiative lifetime, g_i and g_f are the degeneracies of the levels i and f, ν_{if} is the frequency of the transition considered and R_{if} is the matrix element of the dipolar moment of the transition. It can be shown that the Einstein spontaneous emission coefficient is connected to the induced absorption coefficient B_{if} or to the induced emission coefficient B_{fi} by the relation:

$$A_{if} = \frac{8\pi h\nu_{if}^3}{c^3}B_{if} = \frac{8\pi h}{\lambda_{if}^3}B_{if} = 8\pi h\sigma_{if}^3 B_{if} \qquad [1.3]$$

with $\frac{B_{if}}{g_f} = \frac{B_{fi}}{g_i}$ and in which λ_{if} is the wave length and σ_{if} (in cm^{-1}) the wave number associated with the transition between the two levels.

Based on the balanced equation between the levels involved in the transition and by considering the populations of each level such that: $N_i = N_0\, exp\left(-\frac{E_i}{k_BT}\right) = N_0\, exp\left(-\frac{hc\sigma_i}{k_BT}\right)$, as well as the shape of the absorption line (Gaussian by Doppler effect, Lorentz by pressure broadening), the intensity of an absorption vibration–rotation line in gas phase in the infrared range can be written as:

$$S_{if}^g = \int_{\sigma_{\min}}^{\sigma_{\max}} \frac{8\pi^3}{3hc}\sigma_{if} f\left(\sigma - \sigma_{if}\right) N_0 \left[1 - e^{\left(-\frac{hc\sigma_{if}}{k_BT}\right)}\right] g_i \frac{e^{\left(-\frac{hc\sigma_i}{k_BT}\right)}}{Q(T)} R_{if}^2\, d\sigma \qquad [1.4]$$

where σ_{if} is the wave number (in cm^{-1}) of the rotational–vibrational transition considered, N_0 is the number of molecules per volume unit, $hc\sigma_i$ is the energy of the initial level, $Q(T) = \sum_i g_i \exp\left(-E_i/k_BT\right)$ designates the total partition function of the molecule at the temperature T, R_{if} is the rotational–vibrational transition moment and finally g_i is the degeneracy due to the nuclear spin of the initial level. In this formula, the line shape is a Voigt function, the convolution product of a Gaussian by a Lorentzian, because the Doppler effect and the broadening by pressure are concomitant processes and its integral on the absorption domain equals 1 ($\int_{\sigma_{\min}}^{\sigma_{\max}} f\left(\sigma-\sigma_{if}\right)d\sigma=1$).

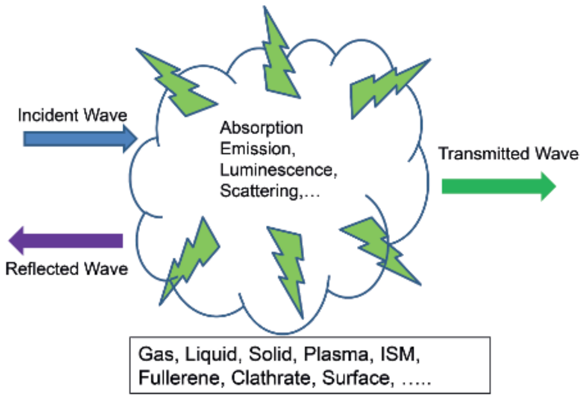

Figure 1.1. *Light–matter interaction*

When the absorption lines corresponding to the transitions between the energy levels can be experimentally determined, either by classical spectroscopy resolved in frequency via an interferometer or by laser absorption by sweeping the absorption spectral domain of the line, one can connect this intensity to the absorption coefficient as determined by the Beer–Lambert law.

The absorption coefficient $\alpha(\omega)$ of a gas probed on a length dz by an electromagnetic wave at the angular frequency ω is expressed as $\alpha(\omega)=\frac{1}{I}\frac{dI}{dz}$, where I is the temporal average of the Poynting vector of the electromagnetic radiation or intensity ($I=\frac{cn}{2}\left|E_0\right|^2$). In QM, its expression is given by: $\alpha(\omega)=\frac{\hbar\omega\Gamma}{PV}$, where P is the Poynting vector representing the flux of the incident electromagnetic wave, V is the volume, Γ is the transition probability per unit time and $\hbar\omega$ is the energy of the absorbed photon. For a transition in gaseous phase, the absorption coefficient $\alpha(\omega)$ as a function of the angular frequency ω depends on the molecule, the transition, the number of molecules, the pressure and the temperature. Experimentally, we can extract these quantities from the integrated intensity of the absorption spectra:

$$S_{if}^{g} = \frac{1}{2lN_0}\int_{\sigma_{\min}}^{\sigma_{\max}} \ln\frac{I_0\left(\sigma-\sigma_{if}\right)}{I_t\left(\sigma-\sigma_{if}\right)}d\sigma = \frac{1}{2lN_0}I_{if} \qquad [1.5]$$

where N_0 is the number of molecules per cm^3, $2l$ is the length traveled by the radiation in the sample and the term contained in the integral is the integrated absorption measured on the IR absorption spectrum domain. Another parameter that enables the absorption to be quantified is the integrated absorption coefficient $S_{if}^{0} = \frac{S_{if}}{P}$, which is expressed relative to the pressure of the surrounding media.

From the observed isolated line profiles that are connected to the molecular transitions of the species present in the planetary atmospheres (*atmos:* vapor; *sphaira:* sphere), it is possible to extract physical parameters such as the pressure, temperature, molecular abundance and the dynamic properties of the atmosphere, such as the wind speed and the circulating currents associated with the movement of chemical species from hot regions to cold ones, for example.

1.1.2. *Diatomic molecules: observation, analysis and interpretation*

Studies based on the spectra and the photographs obtained from observations of the sky, either performed in ground-based observatories or in various space missions, have validated the existence of an atmospheric layer on other planets of the solar system, just like on Earth. For example, in a diatomic molecular form, amongst other major constituents of the planets' atmospheres, one finds dinitrogen N_2 and dioxygen O_2 on Earth and dihydrogen H_2 on Jupiter. On Triton and Titan, the largest satellites of the planets Neptune and Saturn, respectively, the atmosphere is mainly made up of dinitrogen N_2 similar to Earth's atmosphere. The identification of these diatomic species has enabled us to compare the planets' composition and to propose scenarios on the environmental conditions that prevailed when the planets were formed. Giant planets were formed in an environment that essentially contains hydrogen (75% in mass) and helium (24%), a cloud pushed away by solar wind up to the distance of Jupiter and close in composition to the primitive nebula at the origin of the Sun. As for the four telluric planets, they were formed in very similar conditions, based on the same materials, but with a gaseous environment different in composition to that of the primitive nebula.

The negligible quantity of dihydrogen H_2 on telluric planets (Mars, Earth and Venus) in comparison to the Jovian planets (Jupiter and Saturn) is explained by a stronger force of gravity and weaker temperatures of the external layers compared to the telluric planets. Therefore, the external Jovian planets preserved an atmosphere which is close in composition to that of the primitive nebula.

The singularity of the 20% of O_2 in the Earth's atmosphere is attributed to two processes. A physical–chemical process takes place in the high Earth atmosphere by which solar and cosmic radiation breaks down water molecules in dioxygen and dihydrogen. As the dihydrogen definitively escapes into space at an average rate of 3 kg/s, the dioxygen accumulates in the atmosphere. By a biochemical natural process, O_2 is also produced by cyanobacteria, and more generally by green plants that transform carbon dioxide into dioxygen by the mechanism of photosynthesis.

Nitric oxide (NO) emissions can be observed on all telluric planets surrounded by an atmosphere. On Venus, these emissions have been identified with those of O_2 in the high atmosphere of Venus since 1979 [CON 79, FEL 79, STE 79]. These two molecules are detectable because of their aeronomic emissions on the nocturnal hemisphere of the planet. Dioxygen O_2 mainly emits in the infrared range and NO in the ultraviolet range between 180 and 300 nm. It is also possible to detect NO in the near infrared between 1.2 and 1.3 µm. The aeronomic emissions of NO are due to a radiative recombination process, which is produced on the night side of the planet. As Venus's atmosphere is essentially composed of CO_2 and N_2, solar radiation breaks these molecules into free atoms of nitrogen and oxygen on the day side. In the high atmosphere, and above 100 km, the zonal winds transport these atoms toward the nocturnal side where they recombine to form NO in an excited state, which then emits ultraviolet radiation. The aeronomic emission of NO is thus a natural tracer of subsolar/antisolar circulation.

On Mars, the observations from the imaging spectrometer OMEGA on ESA's Mars Express orbiter led to the detection of a dim infrared light above Mars' Winter poles. There again, when the oxygen and nitrogen atoms recombine, an ultraviolet nocturnal light results from the NO formed, as well as an emission in the near infrared (O_2) at 1.27 µm from dioxygen. The detection of the nocturnal telluric emission was observed for the first time in 2010 but it was expected ever since 2005 when the NO emission in Mars' atmosphere was detected by the SPICAM instrument on board Mars Express. The Mars nocturnal fluorescence of O_2 ($a^1\Delta_g$) at 1.27 µm thus detected is due to the recombination of the O atoms formed by the photolysis of CO_2 during the day at higher altitudes at 80 km and transported toward the bottom at the pole by the Hadley circulation. In 2010, the first detections of the nocturnal fluorescence of O_2 ($a^1\Delta_g$) indicated that it is about two orders of magnitude less intense than the daytime fluorescence that has a different source, being due to the photodissociation of the ozone molecule. Similar observations have been made from the Venus Express mission on the fluorescence of the atmosphere of Venus in good correlation with the observations made from the ground base observatories for this planet [BER 12, GER 08, GER 09a, GER 09b, GON 10].

The detection of gaseous matter between some billions of suns of the Milky Way in space has led the scientific community in astrophysics to postulate the existence of an interstellar medium (ISM), which is composed of dense or diffuse molecular clouds or dust grains. In the ISM, which in a laboratory would be considered to be a hypervacuum environment [TEN 03], the gaseous matter exists in different forms of rather cold clouds at temperatures of the order of 20–30 K. The interstellar molecules are formed by chemical reactions in interstellar clouds of gas and interstellar and circumstellar dust. When a molecule is ionized as a result of its interaction with cosmic radiation, the electrically charged ion tends to attract nearby reactants through electrostatic interaction on the dust surfaces.

Among the most abundant diatomic molecules detected one finds dihydrogen H_2 and in molecular clouds, carbon monoxide CO whose presence is revealed by its rotational transition at 2.6 mm. The presence of dihydrogen is expected because the universe is mainly made up of atomic hydrogen and although predicted by A. Eddington as early as in 1926, it was only detected half a century later in 1970 [CAR 70]. In molecular clouds, almost all the hydrogen is under a molecular form. The Copernicus satellite has detected absorption bands of ultra-UV lines of H_2 (Lyman & Werner electronic transition bands) and HD at the beginning of the 1970s.

The first detections of diatomic species in the space surrounding the stars of our galaxy, CH, CH^+ and CN (cyanide embryo), which are very simple molecular species, were made between 1937 and 1941 [ADA 41, MCK 40, SWI 37] in the field of astrophysics, through observations of characteristic absorption lines present in the radiation spectrum of many stars in the ultraviolet and visible ranges. Given the electronic structure of these interstellar species, namely two radicals with dangling valences and a cation, it was difficult to consider them as ordinary chemical products. The presence of CH^+ was confirmed by laboratory experiments, which enabled the cation to be characterized at around 400 nm [DOU 41]. By 1941, diatomic molecules or species had been identified not only in solar and star spectra but also in those of comets, particularly in those observed in the ISM such as OH, C_2, NH, CO^+ and N_2^+, for example.

The analysis of the spectrum attributed to CN [MCK 40] showed structures with initial transition states not only from the fundamental rotational level but also from the first excited level. Moreover, the relative intensities of these lines were consistent with a population distribution of the two levels characterized by a temperature of 2.3 K. However, the cosmological importance of this temperature was not then acknowledged. Thanks to progress in technology that has helped to broaden the electromagnetic observation range of chemical species to include microwave, millimetric and infrared radiation, in 1965, Penzias and Wilson [PEN 65] observed in the microwave range an isotropic radiation that was attributed to the isotropic radiation of a black body at 3.5 K by Dicke *et al.* [DIC 65] (cosmological background radiation (CMBR) currently measured at 2.7 K). The development of radio-telescopes further enabled the detection of molecules, which have a permanent electric dipole moment. In 1960, the spectral absorption lines of the OH radical were observed at 18 cm (OH/H ratio of 10^{-7}) by Weinreib *et al.* [WEI 63] in the Cassiopeia A constellation. In 1970, the CO emission line, $J = 1 \rightarrow J = 0$ at 2.6 mm was detected for the first time by R.W. Wilson, K.B. Jefferts and A.A. Penzias. These diatomic molecules constitute molecular tracers with a wave length in the mm range, which enable probing of the physical conditions in the interstellar clouds (temperature, density of the molecular hydrogen, mass, velocity profiles, etc.) as shown by the pioneering works of Encrenaz *et al*. [ENC 75], Tucker *et al*. [TUC 76] and Dickman [DIC 78].

The technology of receivers and antennas has been continuously improving since the 1980s and numerous complex interstellar molecules have thus been detected, mainly with wavelengths in the millimeter range (the largest molecules are chains containing 13 atoms). The study of the physical–chemical processes in the ISM is paramount to fully understand and correctly interpret the observations from dense and cold molecular clouds, not only in our own galaxy but also in other galaxies, particularly in the case of CO studies. As mentioned in the Preface, progress in technologies enables us to design and build observation instruments (telescopes, LIDAR, spectrometers, interferometers, etc.) on board static or mobile observation platforms in order to probe the Earth's atmosphere and also the universe and follow the evolution of galaxies (NASA's James Webb space telescope for 2018) or even observe the exo-planets, the first days of the universe, supermassive black holes and the mysterious nature of dark matter and dark energy ("European Extremely Large Telescope", for 2024). All these instruments equipped with sensors and other detection systems are designed to match the relevant electromagnetic radiation necessary to investigate galaxies and the universe nearest to regions in space that will be observed and explored. Technologies of connected objects associated with drones and robotics will allow us to increase our observation capacities and data analysis must be supported by theoretical models of non-isolated molecules built on physical grounds and from first principles for relevant and objective interpretation.

1.2. Hamiltonian of a diatomic molecule

Nuclei and electrons are characterized by their masses (m_N and m_e), their charges ($Z_N e$ et $-e$), their spins (I_N and ½), their magnetic moments (μ_N and μ_e) and for nuclei, a quadrupolar moment ($Q^N_{\alpha\beta}$). Given these characteristics, when we consider the different interactions between the nuclei and the electrons, the Hamiltonian of the molecular system can be put in the following form:

$$H = T + V + H_{SF} + H_{shf} \qquad [1.6a]$$

in which

$$T = T_N + T_e = T_{CM} + T_0 + T' \quad [1.6b]$$

$$V = V_{NN} + V_{ee} + V_{eN} \quad [1.6c]$$

$$H_{FS} = H_{SO} + H_{SR} + H_{SS} \quad [1.6d]$$

$$H_{hfs} = H_{IL} + H_{IR} + H_{II} + H_{IS} + H_{EQ} \quad [1.6e]$$

In equation [1.6b], $T_N = \sum_{N=1}^{2} \frac{P_N^2}{2M_N}$ is the kinetic energy operator of the nuclei and $T_e = \sum_{e=1}^{n} \frac{P_e^2}{2m_e}$ is the kinetic energy operator of the electrons. It can be shown that the sum of T_N and T_e can be expressed as the sum of T_{CM}, the kinetic energy of the center of mass (CM), T_0, the kinetic energy of particles inside the molecule and the mass polarization operator, a crossed kinetic term of the form $T' = \frac{1}{2m_N} \sum_{e,e'=1}^{n} P_e P_{e'}$, where P_e is the linear momentum operator of an electron that represents the fluctuations of the position of the CM due to the movement of the electrons and where $m_N = \frac{M_1 M_2}{M_1 + M_2}$ is the reduced mass of the nuclei. A very good discussion of this decomposition can be found in [BRO 03].

Equation [1.6c] represents the Coulomb potential that characterizes the electrostatic interaction between the nuclei (V_{NN}), between the electrons (V_{ee}) and between the electrons and the nuclei (V_{eN}).

Equation [1.6d] (H_{FS}, *FS*: fine structure) describes the interaction of the magnetic moments of the electrons with the intramolecular field that, in the case of a diatomic molecule, is of cylindrical symmetry. The first term H_{SO} (spin-orbit interaction) represents the interaction of the spins of electrons with the magnetic field generated by the orbital movement of the electrons. The second term H_{SR} (spin–rotation interaction) characterizes the interaction of the electrons' spins with the magnetic field generated by the orbital movement of the nuclei. The third term H_{SS} (spin–spin interaction) represents the interaction of the electrons' spins with each other. These terms are responsible for the fine structure observed in the electronic multiplet states of radicals or ions which have a lone electron or the excited or multiplet electronic states of the dioxygen fundamental state, O_2 [BRO 03].

Equation [1.6e] (H_{hfs}, *hfs*: hyperfine structure) describes the interaction of the nuclei's magnetic or quadrupolar moments with the intramolecular field. The first term H_{IL} (spin–orbit interaction) results from the interaction of nuclear spins with the magnetic field generated by the electrons' orbital movement. The second term H_{IR} (spin–rotation interaction) represents the interaction of the nuclear spins with the magnetic field generated by the nuclei's orbital movement. The third term H_{II} (spin–spin interaction) represents the interaction of nuclear spins with each other. The fourth term H_{IS} (spin–spin interaction) characterizes the interaction of the nuclear spins with the electrons' spins and the Fermi contact interaction. The fifth term H_{EQ} results from the interaction between the electric quadrupolar moments of the nuclei and the gradient of the intramolecular electric field. These interactions can be observed in high-resolution spectroscopy in the microwave frequency region.

If one takes the non-sphericity of the distribution of nuclear charges and their movements into account, other electrical and magnetic moments are also present that are represented by terms of the higher order in the expansion of the Hamiltonian.

As the Hamiltonian matrix is infinite, the exact resolution of the Schrödinger eigenvalues equation (equation [1.1]) is generally impossible. To determine the energy levels of a diatomic molecule, it is necessary to simplify the Hamiltonian.

By a judicious choice of the axes system, the Hamiltonian can be expressed in a form that allows the variables to be separated:

$$H_0 = H - H' = T_{CM} + H_{eVR} + H_{SS} + H_{II}, \quad [1.7]$$

where H' represents the coupling terms and $H_{eVR} = H_e + H_V + H_R$ is the sum of Hamiltonians relative to the electrons and the nuclei's vibration and rotation movements.

The wave functions and the eigenenergies can then be expressed as follows:

$$\left|\Psi_0\right\rangle = \left|\Psi_{CM}\right\rangle \times \left|\Psi_e\right\rangle \times \left|\Psi_V\right\rangle \times \left|Jm_J\right\rangle \times \left|Sm_s\right\rangle \times \left|Im_I\right\rangle \qquad [1.8]$$

$$E_0 = E_{CM} + E_e + E_V + E_R + E_{SS} + E_{II}, \qquad [1.9]$$

where $\Psi_{CM} = \left\langle R_{CM} \middle| \Psi_{CM} \right\rangle$ is the wave function associated with the translation movement of the CM represented by a plane wave, $\Psi_e = \left\langle ..., r_e, ... \middle| \Psi_e \right\rangle$ is the wave function associated with the movement of the electrons that depends on the electrons' position, $\Psi_V = \left\langle q \middle| \Psi_V \right\rangle$ is the wave function associated with the vibration movement of the nuclei around their equilibrium position and that depends on the normal coordinate q (section 2.2.2 of Chapter 2), $\Psi_R = \left\langle \theta, \phi \middle| Jm_J \right\rangle$ is the wave function associated with the rotation movement of the overall molecule around its CM (section 2.2.2 of Chapter 2) and $\left|Sm_s\right\rangle$ and $\left|Im_I\right\rangle$ the wave functions of the electronic and nuclear spins, respectively.

In a first approximation, the molecule's energy is a sum of terms relating to the different degrees of freedom, which are translational (for the CM), electronic, vibrational and rotational (for classical ones) or electronic and nuclear spins (for quantum ones). No approximation is necessary for separating the movement of the CM (first Eckart conditions: the origin of the frame tied to the molecule is placed at the CM) and the spins' degrees of freedom. However, the decomposition of $H_{eVR} = H_e + H_V + H_R$ requires the application of BO approximation or the adiabatic approximation, which allows the nuclei's movements to be separated from those of the electrons. This approximation relies on the ratio of the masses of an electron and a proton (m_e/m_N~1/1,836), which justifies that the nuclei's movement is slower than those of the electrons under the effect of forces of the same order of magnitude. The electronic movement may then be processed for a fixed position of the nuclei.

The exact expression of the rovibronic wave function is given by:

$$\left|\Psi_{eVR}\right\rangle = \left|\Psi_e\right\rangle \left(\left|\Psi_V\right\rangle \left|\Psi_R\right\rangle + \left|\Psi_{VR}\right\rangle \right) + \left|\Psi_{eN}\right\rangle \qquad [1.10]$$

where $\left|\Psi_{VR}\right\rangle$ is associated with the interaction between the vibration and the rotation and $\left|\Psi_{eN}\right\rangle$ with the interaction between the movement of the electrons and that of the nuclei. When these interactions are neglected, the wave function can be expressed as a product of the individual wave functions (equation [1.8]), the electronic wave function then depending parametrically on the internuclear distance.

The molecular energy variation corresponding to a transition between two energy levels is written for the rovibronic part as follows:

$$\Delta E_{eVR} = \Delta E_e + \Delta E_V + \Delta E_R \qquad [1.11]$$

with $\Delta E_e >> \Delta E_V >> \Delta E_R$ (Figure 1.2), which corresponds to the electronic levels that are relatively spaced in comparison to the vibrational sublevels; the latter are themselves more spaced than the rotational sublevels.

These scales of magnitude enable the spectra to be classified into three categories:

– the rotation spectra in which the electronic energy and the vibration energy are unchanged ($\Delta E_e = 0$ and $\Delta E_V = 0$). The spectrum is shaped in lines, which are each associated with a value of ΔE_R;

– the vibration–rotation spectra in which the electronic energy is unchanged ($\Delta E_e = 0$). The spectrum is shaped in bands which are each associated with a value of ΔE_V. Each band is composed of lines associated with the different values of ΔE_R;

– the electronic spectra comprised of different systems of bands that are each associated with a value of ΔE_e. The bands of the same system correspond to different values of ΔE_V. Each band is composed of lines associated with the values of ΔE_R.

The rotation spectra are observed in the microwave and far-infrared ranges (between 25 and 1,000 µm or 400 and 10 cm^{-1}); the vibration–rotation spectra in the mid-infrared range (between 2.5 and 25 µm or 4,000 and 400 cm^{-1}) or near-infrared range (between 0.75 and 2.5 µm or 13,333 and 4,000 cm^{-1}); the electronic spectra in the near-infrared, visible or ultraviolet range. The time scales corresponding to these degrees of freedom are located between 0.1 and 1 fs for the electrons, between 10 and 100 fs for the vibration and between 0.1 and 10 ps for the rotation.

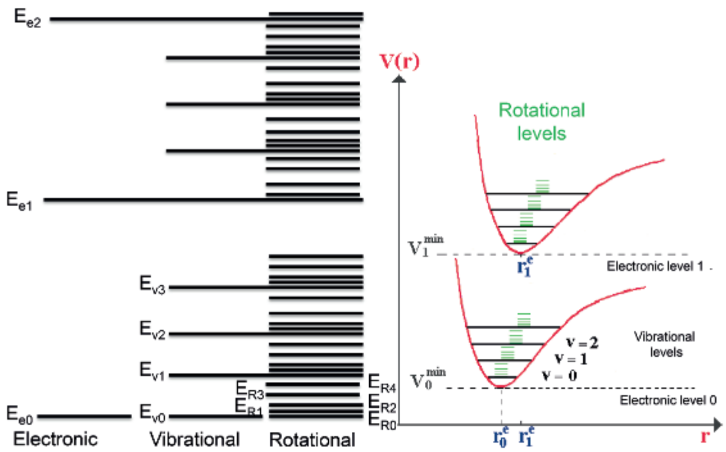

Figure 1.2. *Diagram of the electronic, vibrational and rotational energies of a molecule*

1.3. Symmetry properties of a diatomic molecule

1.3.1. *Group of symmetry*

A diatomic molecule may form in the gaseous phase when the electrons that are initially localized on each of the atoms are shared, resulting in a molecule's bonding state for an approximate distance corresponding to the molecule's bond length.

If one looks at a diatomic molecule's rovibronic degrees of freedom, comprising n electrons, the most general movement depends on $6 + 3n$ position coordinates. If we discard the three translation degrees of freedom (T_{CM}) of the CM which are not involved in the study of rovibronic spectra, this number is reduced to $3 + 3n$ coordinates, namely:

– $3n$ electronic coordinates;

– 6 – 5 = 1 vibrational coordinates (5:3 for the translation and 2 for the rotation);

– two rotational coordinates.

We represent a molecule by defining a geometric figure corresponding to the equilibrium configuration of the two nuclei. The reference system connected to the equilibrium configuration (section 2.2 of Chapter 2) is chosen so that its origin is at the CM (first Eckart condition) and its axes along the principal directions of inertia of the equilibrium configuration. In the case of a diatomic molecule and a general linear molecule, the axis z is aligned on the internuclear axis and the two other axes are chosen to be perpendicular to z and to each other and have an arbitrary orientation. At a given instant, the configuration that corresponds to the physical situation differs from the reference configuration, which is arbitrarily set. The movement of the two nuclei is decoupled into two movements: a block rotation of the reference configuration (xyz mobile frame moving with the molecule) with respect to a fixed frame (laboratory-fixed referential, $(O,\vec{X},\vec{Y},\vec{Z})$) defined by two Euler angles θ and φ (section 2.3.2 of Chapter 2) and the vibration defined by the instantaneous positions of the two nuclei with respect to their equilibrium position. The axis of the reference configuration coincides with the axis of the instantaneous configuration and the vibration is described by a normal coordinate q (section 2.2.2 of Chapter 2) equal to the product of the bond length by the square root of the reduced mass.

A diatomic molecule's symmetry properties are determined with reference to the symmetry point group of the nuclei's equilibrium configuration [AMA 80a, CAM 88, LAN 75, WIL 80]. First, we define a reference system connected to the equilibrium configuration and which moves with it. We then establish the symmetry point group by identifying the different possible reference system's changes for which the equilibrium configuration is superimposed. The operations that bring about such changes are the symmetry operations.

The configuration of the homonuclear diatomic molecules A_2, with identical atoms, comprises indiscernible nuclei (A, A). Its corresponding point group $D_{\infty h}$ (Table 1.1) comprises the following symmetry operations (Figure 1.3):

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

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

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

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

The symmetry elements of A_2 are, respectively, the rotation axis of the first kind z (proper axis that includes the identity), the rotation axes t, the symmetry planes zt and the rotation axis of the second kind z (improper axis that includes the inversion).

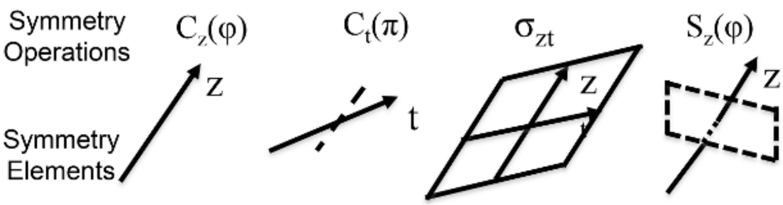

Figure 1.3. *Symmetry operations (Schoenflies notation) and symmetry elements of a homonuclear diatomic molecule*

	I	*2C∞(φ)*	*∞σV*	*I*	*2S∞(φ)*	*∞C2*	
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 1.1. *Symmetry Group $D_{\infty h}$: table of characters*

For the heteronuclear molecules AB, with distinct atoms, the symmetry point group $C_{\infty v}$ (Table 1.2) comprises the following symmetry operations:

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

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

The symmetry elements of AB are, respectively, the rotation axis of the first species z and the symmetry planes zt.

	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	$2\cos\varphi$	0	(μ_X, μ_Y) (T_X, T_Y) (J_X, J_Y)
Δ	2	$2\cos\varphi$	0	
Φ	2	$2\cos\varphi$	0	

Table 1.2. *Symmetry group $C_{\infty V}$: table of characters*

The definition of the symmetry types of the groups $C_{\infty v}$ and $D_{\infty h}$ is connected to the behavior of the physical quantities and the other molecular properties with respect to the symmetry operations. The symbols Σ, Π, Δ… are related to the behavior with respect to the rotation $C_z(\varphi)$; there are two one-dimensional irreducible representations with totally symmetric cylindrical symmetry (Σ) and the others, which are all two-dimensional, are in an infinite number ($\Pi,\Delta,\Phi,\ldots$); the sign + or – added as a superscript to a symbol Σ (electronic distribution possessing the cylindrical symmetry around z or invariant states in a rotational symmetry operation around z) is related to the symmetric or antisymmetric character with respect to a reflection σ_{zt}. For the group, $D_{\infty h}$, the index g (gerade or even) or u (ungerade or uneven) is related to the symmetric or antisymmetric character with respect to the inversion. The symmetry operations of the group $D_{\infty h}$ are twice those of the group $C_{\infty V}$ as a result of the existence of the inversion operation.

As a result, the irreducible representations of the symmetry point group of the diatomic molecule, homonuclear molecule ($D_{\infty h}$) or heteronuclear molecule ($C_{\infty v}$), are, respectively, designated by $\Sigma_g^+, \Sigma_u^+, \Sigma_g^-, \Sigma_u^-$, $\Pi_g, \Pi_u, \Delta_g, \Delta_u, \Phi_g, \Phi_u, \Gamma_g, \Gamma_u$.... and $\Sigma^+, \Sigma^-, \Pi, \Delta, \Phi, \Gamma$.... and are used to highlight and thus identify the symmetry properties of the rovibronic states.

The symmetry of the states bear particular significance on the possible transitions that may take place between the quantum states and which are responsible for the spectra observed. A transition between two quantum states takes place if at least one of the integrals of the type:

$$R_{mn} = \left\langle \Psi_{eVR}^{m} \middle| R \middle| \Psi_{eVR}^{n} \right\rangle = \int \Psi_e^{m*} \Psi_V^{m*} \Psi_R^{m*} R \Psi_e^n \Psi_V^n \Psi_R^n d\tau \qquad [1.12]$$

is different from zero and is therefore symmetric with respect to the symmetry operations, which leave the molecule invariant. This is equivalent to saying that $\Gamma(|\Psi_m\rangle) \otimes \Gamma(|\Psi_n\rangle) \otimes \Gamma(R)$ must contain the unity representation, that is 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.

In infrared spectroscopy, corresponding to the absorption or emission of photons (absorption or emission spectroscopy), the operator R is one of the components (μ_x, μ_y, μ_z) of the electric dipole moment (sections 2.2.3, 2.3.3, and 2.4.2 of Chapter 2). In elastic diffusion (Rayleigh, Mie) or inelastic diffusion (Raman, Brillouin), R is one of the operators connected to the elements $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{yz}, \alpha_{xz}$ of the molecule's polarizability tensor. The component of the permanent electric dipole moment μ_z of a heteronuclear diatomic molecule is of the type Σ^+. The electric dipole moment induced by the vibration (section 2.2.3 of Chapter 2) has the same symmetry as that of the power of the vibration normal coordinate, which is also of the type Σ^+.

The homonuclear diatomic molecules have no permanent or induced electric dipole moment and therefore do not have a vibration–rotation spectrum. This situation implies that the molecular detection based on rotational transitions does not apply to hydrogen, for example. However, there is so much hydrogen present in the universe that, although the quadrupolar transitions are weak, the corresponding spectrum is detectable, like that observed in the region of Orion where stars are formed.

1.3.2. *Symmetry of the electronic states*

To label the electronic states of a diatomic molecule, one uses the same convention as for the atoms, with Latin or Greek letters in upper case $(\vec{L},\vec{S},\Sigma,\Pi,\Delta..)$ to characterize all the electrons and in lower case $(\vec{l},\vec{s},\sigma,\pi,\delta...)$ to characterize an electron individually [AMA 80a, AMA 80b, HER 50, HOL 86, LAN 75].

In an atom, the orbital angular momentum $\vec{L}$ of all the electrons keeps a fixed direction in space due to the spherical symmetry of the nucleus' force field (Figure 1.4(a)). In a diatomic molecule, the force field possesses a cylindrical symmetry around the internuclear axis z and consequently, the orbital angular momentum $\vec{L}$ of all the electrons precesses around z just like an atom placed in an electrical field (Figure 1.4(b)). The projection of $\vec{L}$ on z is equal to $\hbar M_L$ with $M_L = -L,-(L-1),.......,(L-1),L$. L is a quantum number that is connected to the modulus of $|\vec{L}|$ equal to $\hbar\sqrt{L(L+1)}$. Two states with values $\hbar M_L$ and $\hbar M_L^{'}$ have the same energy, which thus depends on the value $\Lambda = |M_L|$. The orbital angular momentum of the electrons is therefore characterized by the axial vector $\vec{\Lambda}$ directed along the z axis, that is the component of $\vec{L}$ along z, rather than $\vec{L}$ itself. Depending on the values of $\Lambda = 0,1,2,3...$, the electronic state is designated by $\Sigma,\Pi,\Delta,\Phi...$. A state Σ is not degenerate, whereas the states $\Pi,\Delta,\Phi...$ are doubly degenerate.

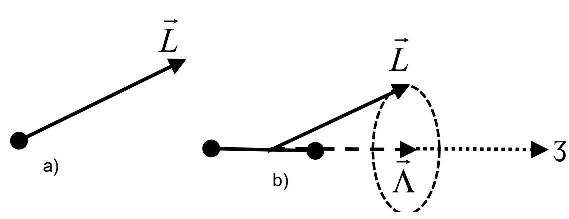

Figure 1.4. *Angular momentum of the electrons: a) atomic and b) diatomic*

The total spin of all the electrons noted $\vec{S}$ is not perturbed by an electrical field but only by a magnetic field. In a state Σ, the orbital movement has no magnetic moment so that the magnetic field is zero, which means that $\vec{S}$ remains fixed in space. In a state $\Pi, \Delta, \Phi \ldots$, the orbital movement of the electrons gives rise to a magnetic field parallel to z. A precession of $\vec{S}$ around z (Figure 1.5) then follows. The projection of $\vec{S}$ on z is equal to $\hbar S_z$ with $S_z = -S, -(S-1), \ldots\ldots, (S-1), S$. S is the quantum number that is connected to the modulus of $|\vec{S}|$ equal to $\hbar\sqrt{S(S+1)}$. For each value of S, there are $(2S+1)$ values of S_z. The precession is due to a magnetic coupling and states corresponding to the opposite values of S_z possess different energies. The quantum numbers S and S_z take integral or half-integral values depending on whether the molecule contains an even number or an odd number of electrons (to avoid confusion, we use S_z instead of Σ as is customary).

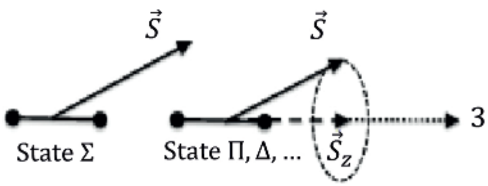

Figure 1.5. *Spin of electrons for different electronic states (Σ, Π, Δ …)*

The total angular momentum of the electrons is obtained by the addition of $\vec{L}$ and $\vec{S}$. Its projection on the z axis is equal to $\hbar\Omega$, such that $\Omega = |\Lambda + S_z|$ (Figure 1.6). Ω takes integral or half-integral value just like S_z depending on whether the molecule contains an even or odd number of electrons. An electronic state is represented by the symbol $^{2S+1}[\Gamma]_{\Lambda+S_z}$, where $[\Gamma]$ designates the symbol $\Sigma, \Pi, \Delta, \Phi, \ldots$ associated with the value 0, 1, 2 or 3 of Λ, respectively. The definition of a state is completed by the multiplicity 2S+1 at the left superscript and at the right subscript by the projections of the total angular momentum of the electrons. For each value of Λ and S , there are $2S+1$ states corresponding to the different values of S_z, which define the orientations of $\vec{S}$ with respect to $\vec{\Lambda}$ and which correspond to the multiplicity of the electronic term.

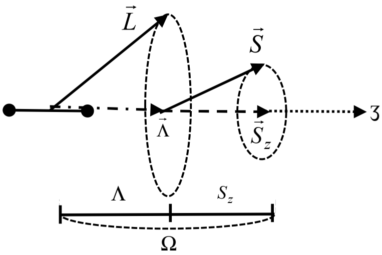

Figure 1.6. *Angular orbital momentum and spin of electrons and total angular momentum of the electrons*

For example, for $\Lambda = 0$ and $S = 1$, we have $S_z = -1, 0, +1$ (multiplicity of 3), and $\Lambda + S_z = -1, 0, +1$. The electronic term is a triplet $^3\Sigma$ whose components are noted as $^3\Sigma_{-1}, {}^3\Sigma_0, {}^3\Sigma_1$. For $\Lambda = 1$ and $S = 1/2$, we have $S_z = -1/2, +1/2$ (multiplicity of 2) and $\Lambda + S_z = +1/2, +3/2$. The electronic term is a doublet $^2\Pi$ whose components are noted as $^2\Pi_{1/2}, {}^2\Pi_{3/2}$ (Figure 1.7).

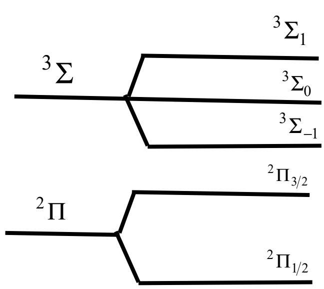

Figure 1.7. *Electronic states and multiplicities*

The symbols $\Sigma, \Pi, \Delta, \Phi, ...$ can be defined from the molecule's symmetry properties without reference to the angular momentum value Λ. The states

Ψ, which are invariant in a rotational symmetry operation of an angle φ around the axis z, are of the type Σ. The other states are doubly degenerate and are studied in pairs $\{\Psi_{-1},\Psi_{+1}\}$. The trace *Tr* of the square matrix 2 × 2, of a rotational symmetry operation of angle φ around the axis z of the basis $\{\Psi_{-1},\Psi_{+1}\}$ allows the symmetry type of the doubly degenerate states to be defined. This trace is expressed as $Tr = 2\cos m\varphi$ and following the value of $m = 1,2,3,\ldots$, the states $\{\Psi_{-1},\Psi_{+1}\}$ are of the type $\Pi,\Delta,\Phi,\ldots$. Depending on whether the function is symmetric or antisymmetric with respect to the reflection symmetry operations of the plane containing the internuclear axis and in the case of a homonuclear diatomic molecule, with respect to the center of symmetry, the states are distinguished by the use of symbols +, – and g, u, respectively.

1.3.3. *Symmetry of the total wave functions*

The molecular states are described by total wave functions that are, in a first approximation, the product of translational, electronic, vibrational, rotational and spin wave functions (equation [1.8]: $|\Psi_0\rangle = |\Psi_{CM}\rangle \times |\Psi_e\rangle \times |\Psi_V\rangle \times |Jm_J\rangle \times |Sm_s\rangle \times |Im_I\rangle$). Because of the first Eckart condition, with the origin of the mobile frame at the nuclear CM, the overall translation of the molecule is not considered, which allows the translational degrees of freedom to be rigorously separated from the other ones.

The electronic wave function $|\Psi_e\rangle$ depends on the electrons' position coordinates ($\langle \vec{r}_e | \Psi_e \rangle$), the vibration wave function $|\Psi_V\rangle$ depends on the vibration's normal coordinate ($\langle q | \Psi_V \rangle$), a linear combination of the weighted Cartesian displacements of the nuclei, the rotation wave function $|\Psi_R\rangle \equiv |J,M\rangle$ depends on Euler angles ($\langle \theta,\varphi | J,M \rangle$) and the nuclear spin's wave function, which is of quantum nature, depends on the nucleus' mass number M (even M: integral spin obeying the Bose–Einstein statistics; odd M: half-integral spin obeying the Fermi–Dirac statistics) (Table 1.6).

To determine the symmetry of an electronic or vibrational wave function, one must know how the electrons' coordinates and the vibrational normal coordinate transform in a symmetry operation [AMA 80a, CAM 88, LAN 75, WIL 80]. In that case, the symmetry operation is defined as a change in the xyz reference frame accompanied by a permutation of the indices that label identical nuclei. The reference system is rotated with respect to the nuclei's equilibrium or instantaneous configuration.

In a diatomic molecule, the internal electrons are localized around each of the molecule's nuclei on complete shells: the orbital angular momentum and the spin momentum are then equal to zero. The valence electrons that contribute to the chemical bond are generally grouped into pairs with parallel spins ($S = 0$) on the orbitals, which have an orbital angular momentum equal to zero ($\Lambda = 0$). The fundamental state is a singlet ($^1\Sigma$), although there are exceptions to this rule, such as for nitrogen monoxide NO, a heteronuclear diatomic molecule whose fundamental electronic level is a doublet $^2\Pi$ ($\Lambda = 1$ and $S = 1/2$), and dioxygen O_2, a homonuclear diatomic molecule, whose fundamental electronic state is a triplet $^3\Sigma$ ($\Lambda = 0$ and $S = 1$). In this case, it is shown that the fundamental electronic state of a stable molecule is totally symmetric with respect to the symmetry operations of a diatomic molecule, and thus either of the type Σ (heteronuclear) or of the type Σ_g^+ (homonuclear). For NO, the state is of the type Π and for O_2, it is of the type Σ_g^- (Table 1.3). The lowest vibrational level is always totally symmetric because the vibrational wave function depends on the internuclear distance, which is invariant with respect to all the group's symmetry operations, that is of the type Σ (heteronuclear) or of the type Σ_g^+ (homonuclear) (Table 1.3).

Symmetry of the fundamental level	Homonuclear group $D_{\infty h}$	Heteronuclear group $C_{\infty V}$
Electronic	Σ_g^+ Except O_2 (Σ_g^-)	Σ^+ Except NO (Π)
Vibrational	Σ_g^+	Σ^+

Table 1.3. *Symmetry type of the electronic or vibrational fundamental state*

In the case of rotation, the equilibrium or instantaneous configuration of the nuclei (the object) is rotated with respect to the XYZ fixed reference system. For molecules belonging to the symmetry group $D_{\infty h}$, the exchange effect should also be considered with respect to the identical nuclei and is determined by rotating the reference frame tied to the equilibrium configuration around the y axis. This operation must be performed in the three subspaces, electronic, vibrational and rotational. In the electronic and vibrational subspaces, the reference system is changed (symmetry operation $C_y(\pi)$) without modifying the object studied, that is the instantaneous configuration of the electrons and the nuclei.

Symmetry operation	Level	Character
$C_y(\pi) \equiv \sigma_{zx} \bullet i$	Vibrational Σ_g^+	Ψ_V symmetric
$C_y(\pi)$	Electronic Σ_g^+ Electronic Σ_u^-	Ψ_e symmetric
$C_y(\pi)$	Electronic Σ_u^+ Electronic Σ_g^-	Ψ_e antisymmetric
$C_y(\pi)$	Even rotational J Odd rotational J	Ψ_R symmetric Ψ_R antisymmetric

Table 1.4. *Symmetry type of the electronic, vibrational and rotational level with the exchange of the two identical nuclei*

In the case of rotational subspaces, the studied object (equilibrium configuration of the nuclei) is rotated without modifying the XYZ fixed reference system. Consequently, the xyz system plays the role of the reference system in the electronic and vibrational subspaces, and in the rotational subspace, that of the studied object (Table 1.4). We use the symbols "s" and "a" to characterize the rotational levels symmetric and antisymmetric with respect to the exchange of identical nuclei.

Another type of characterization is applied to all diatomic (or linear) molecules which either belong to the $C_{\infty v}$ symmetry group or to the symmetry $D_{\infty h}$ group. The total wave function $\left|\Psi_t\right\rangle$ is labeled with the index "+" or "-" depending on whether it remains invariant or changes sign when the xyz reference frame (right-handed) is replaced by a frame in the opposite direction (left-handed). In this case, we perform the symmetry operation σ_{zx} in the electronic or vibrational subspaces. In the rotational subspace, this operation is not possible. In this case, the fixed XYZ frame and the mobile frame xyz must be simultaneously inverted, which is impossible. Then the symmetry operation $C_y(\pi)$ must be applied to the mobile frame xyz (the fixed XYZ frame having been inverted). It can be verified that the operation $C_y(\pi)$ transforms the Euler angles (section 2.3 of Chapter 2) such as: $\theta \rightarrow \pi - \theta$ and $\phi \rightarrow \phi + \pi$. The rotational wave function $|\Psi_R\rangle$ transforms in the following way $(-1)^J|\Psi_R\rangle$, meaning that it is invariant if J is even and changes sign for odd J (Table 1.5).

Symmetry operation	Homonuclear Group $D_{\infty h}$	Heteronuclear Group $C_{\infty V}$	Character
σ_{zx}	Vibrational Σ_g^+	Vibrational Σ^+	Ψ_V symmetric
σ_{zx}	Electronic Σ_g^+ Electronic Σ_u^+	Electronic Σ^+ Electronic Σ^+	Ψ_e symmetric
σ_{zx}	Electronic Σ_g^- Electronic Σ_u^-	Electronic Σ^- Electronic Σ^-	Ψ_e antisymmetric
$C_y(\pi)$	Even rotational J Odd rotational J	Ψ_R symmetric Ψ_R antisymmetric	Ψ_R symmetric Ψ_R antisymmetric

Table 1.5. *Symmetry type of the electronic, vibrational and rotational level in an inversion operation of the xyz frame*

These symmetry properties are useful for obtaining the selection rules in emission or absorption spectroscopy, on the one hand, and in Raman diffusion spectroscopy, on the other hand, and thus to determine the relevant technique to use in order to detect a diatomic molecule. In absorption or emission spectroscopy, it is shown that the transitions are only possible between states of different symmetry ($+ \leftrightarrow -$) and that in Raman diffusion spectroscopy the transitions are only possible between states of the same symmetry ($+ \leftrightarrow + \; or \; - \leftrightarrow -$).Thus, for homonuclear molecules, only the Raman diffusion is possible with transitions between states of the same symmetry ($s \leftrightarrow s \; or \; a \leftrightarrow a$) corresponding to a variation of the quantum number J, which must be even ($\Delta J = 2$). Symmetry properties show that it is impossible to observe the pure rotation spectrum in emission or absorption for a homonuclear diatomic molecule.

To analyze the sprectra observed in emission (respectively in absorption), and in Raman diffusion, it is necessary to take into account the spins of the electrons and of the nuclei by considering the total wave function (equation

[1.8]) to establish selection rules. Generally, this wave function is written by including the spin variables of electrons in the electronic wave function, such that only the exchange effect of the identical nuclei on the symmetry of the total wave function needs to be considered. The wave function is then written under the form: $|\Psi_t\rangle = (|\Psi_e\rangle \times |Sm_s\rangle \times |\Psi_V\rangle \times |Jm_J\rangle) \times |\mathrm{Im}_I\rangle$. It is obvious that only the spectra of homonuclear molecules will show structures that are directly connected to the possibility of exchanging the identical nuclei in the molecule. This effect may be determined by using the permutation operator properties of the two particles. In a permutation operation, the total wave function may be invariant or may change its sign, which corresponds to the two eigenvalues –1 and +1 of the permutation operator of the two particles. The wave functions can be grouped into "*s*" states and "*a*" states depending on whether the wave function is symmetric (+1) or antisymmetric (–1) in a permutation operation of indiscernible particles. The effect of the operator *O* associated with the physical quantity that induces the transition between two states, resulting in the spectra that are observable in emission or absorption spectroscopy (electric dipole moment, electric quadrupole moment, magnetic dipole moment), in Raman diffusion spectroscopy (polarizability) or in collision spectroscopy (collision operator) can be calculated from the transition moment $\langle \Psi_t' | O | \Psi_t'' \rangle$. It is shown that because the operator *O* is invariant in an exchange operation of two identical particles, the product $\langle \Psi_t' | \Psi_t'' \rangle$ must also be invariant which implies that $|\Psi_t'\rangle$ and $|\Psi_t''\rangle$ are either both symmetric or both antisymmetric. Consequently, a system that is initially in a symmetric state or in an antisymmetric state remains as such. The states may thus be grouped into two categories.

In the case of the exchange of two electrons in one atom, a state $|\Psi_t\rangle$ is always antisymmetric according to the Pauli principle, which stipulates that two electrons cannot be found in states characterized by identical values of all the quantum numbers. Two electrons on the same orbital (same space variables) must have different spin orientations ($\pm 1/2$). In the case of a nucleus of mass number M which contains M particles of spin $1/2$, exchanging two nuclei amounts to exchanging M times particles of spin $1/2$. The wave function $|\Psi_t\rangle$ changes sign each time the two particles are exchanged, so that $|\Psi_t\rangle$ is symmetric or antisymmetric depending on whether M is even or odd. The nuclear spin wave function which is of quantum origin depends on the nucleus' mass number M (even M: integral spin obeying the Bose–Einstein statistics; odd M: half-integral spin obeying the Fermi–Dirac statistics) (Table 1.6). These different properties are responsible for the structures present in the IR and Raman spectra of the homonuclear diatomic molecules.

In the case of a homonuclear diatomic molecule A-A, the nuclear spin wave function can be put under the form of a product: $|\Psi_I\rangle = |\Psi_i^{(1)}\rangle \times |\Psi_j^{(2)}\rangle$, an expression which is interpreted with the nucleus numbered 1 in the spin state *i* and the nucleus numbered 2 in the spin state *j*. The states *i* and *j* are characterized by the value of the quantum number I_z which may take $2I+1$ values ($-I$, $-(I-1)$, etc., $I-1$, I), where *I* designates the nucleus' spin.

For example for $I = 0$, we have $I_z = 0$, and the wave function is written as: $|\Psi_I\rangle = |\Psi_0^{(1)}\rangle \times |\Psi_0^{(2)}\rangle$. This wave function is symmetric in the exchange of nuclei.

For $I = 1/2$, we have $I_z = -1/2, +1/2$. Therefore, four wave functions can be written (multiplicity of 4): $|\Psi_1\rangle = |\Psi_{1/2}^{(1)}\rangle \times |\Psi_{1/2}^{(2)}\rangle$, $|\Psi_2\rangle = |\Psi_{1/2}^{(1)}\rangle \times |\Psi_{-1/2}^{(2)}\rangle$, $|\Psi_3\rangle = |\Psi_{-1/2}^{(1)}\rangle \times |\Psi_{1/2}^{(2)}\rangle$ and $|\Psi_4\rangle = |\Psi_{-1/2}^{(1)}\rangle \times |\Psi_{-1/2}^{(2)}\rangle$. The wave functions $|\Psi_1\rangle$ and $|\Psi_4\rangle$ are symmetric. From the two other wave functions, $|\Psi_2\rangle$ and $|\Psi_3\rangle$, two other wave functions can be formed, one of which is symmetric, $|\Psi_s\rangle = 1/\sqrt{2}\left(|\Psi_2\rangle + |\Psi_3\rangle\right)$ and the other which is antisymmetric $|\Psi_a\rangle = 1/\sqrt{2}\left(|\Psi_2\rangle - |\Psi_3\rangle\right)$. Therefore, when $I = 1/2$, four wave functions are obtained, three symmetric and one antisymmetric.

Statistic	Number of mass M	Nuclear spin	Character
Bose–Einstein	Even	Integral	C_t symmetric
Fermi–Dirac	Odd	Half-integral	C_t antisymmetric

Table 1.6. *Nuclei's statistics of the even and odd mass number and wave function symmetry*

In general, it can be shown that for a nucleus' spin *I*, there are $(2I+1)(I+1)$ symmetric functions and $(2I+1)(I)$ antisymmetric functions. The symmetric states are called *ortho* states and the antisymmetric states are called *para* states. There are always more *ortho* states than *para* states. When $I = 0$, there is no *para* state. A state can also be characterized from the addition of the spins of each nucleus that we label *T,* such that $|I_1 - I_2| \le T \le |I_1 + I_2|; (T = 0, 1, ...2I)$ and the projection of *T* on the internuclear axis $-T \le M_T \le +T;\ \Delta M_T = +1$. It is shown that the *ortho* states correspond to the even *T* states and the *para* states correspond to the odd *T* states, which are valid, regardless of the statistics: Bose–Einstein or Fermi–Dirac.

When one considers the total wave function $|\Psi_t\rangle = |\Psi_{eVR}\rangle |\Psi_I\rangle$, the product must be symmetric if the nuclei obey the Bose–Einstein statistics and must be antisymmetric if the nuclei obey the Fermi–Dirac statistics. As a result, the relative statistical weight of the $|\Psi_{eVR}\rangle_s$ states of the "*s*" type and the $|\Psi_{eVR}\rangle_a$ states of the "*a*" type depend on this property. We have $\frac{|\Psi_{eVR}\rangle_s}{|\Psi_{eVR}\rangle_a} = \frac{I+1}{I}$ if the nuclei obey the Bose–Einstein statistics and $\frac{|\Psi_{eVR}\rangle_s}{|\Psi_{eVR}\rangle_a} = \frac{I}{I+1}$ if the nuclei obey the Fermi–Dirac statistics. If $I = 0$, only the states $|\Psi_{eVR}\rangle_s$ are present.

These results are summarized in Table 1.7.

Statistics	Ψ_{eVR}	Ψ_I	Statistical weight
Bose–Einstein (*I* integer) Ψ_t symmetric	*s* *a*	*ortho* *para*	(2*I*+1)(*I*+1) (2*I*+1)*I*
Fermi–Dirac (*I* half-integer) Ψ_t antisymmetric	*s* *a*	*para* *ortho*	(2*I*+1)*I* (2*I*+1)(*I*+1)

Table 1.7. *Statistic weight of the "s" and "a" states for the nuclei with even and uneven mass number*

As the character "*s*" or "*a*" of the states depends on the parity of the rotational quantum number *J*, there is a correspondence between (*s, a*) and (even *J*, odd *J*), which depends on the symmetry type of the fundamental electronic level (Table 1.5). The rotational sublevels have different statistical weights depending on whether the *J* is even or odd.

For example, for the diatomic molecules N_2, D_2, H_2, and O_2, the exchanged spins are, respectively, 1 for N and D, 0 for O and ½ for H. For N_2, which has a fundamental electronic state of the Σ_g^+ type, the even *J* levels are "*s*" and odd *J* are "*a*". As the spin of N is equal to 1, the "*s*" levels are *ortho* and the "*a*" levels are *para*. As the ratio of the statistical weight of *s/a* is equal to 2/1 (Table 1.7), the even *J* levels are twice as populated as the odd *J* levels. We have the same result for D_2. For H_2, the fundamental electronic state is of the Σ_g^+ type, but the nuclei obey the Fermi-Dirac statistics, and the "*s*" levels are *para* and the "*a*" levels are *ortho*. As the ratio of the statistical weight *s/a* is equal to 1/3 (Table 1.7), this time the odd *J* levels are three times as populated as the even *J* levels. For O_2, the fundamental electronic state is of the Σ_g^- type (antisymmetric: Table 1.5) and as the nuclear spin is zero, only the *ortho* states are present and consequently only the odd *J* levels are populated (Table 1.5).

These symmetry considerations show that in the rotational Raman spectrum (LIDAR spectroscopy) of homonuclear diatomic molecules, the series of lines called Stokes and the series of lines called anti-Stokes have intensity alternations; one line out of two is more intense than its neighbor. For instance, in the N_2 spectrum, the lines corresponding to even *J* are twice as strong as the lines corresponding to odd *J*. For H_2, the lines corresponding to odd *J* are three times stronger than the even *J* lines. For O_2, the lines with even *J* are missing in the spectrum.

1.4. Example of the diatomic molecule with two electrons H_2, HD, D_2

1.4.1. *Hamiltonian of the isotopologues*

The most abundant molecule in the universe is dihydrogen. This is the simplest neutral molecule, composed of two nuclei and two electrons. This molecule is homonuclear and therefore belongs to the symmetry group

($D_{\infty h}$). If one considers the isotopologues with the deuterium D nucleus, the HD species is from the symmetry group ($C_{\infty v}$), whereas D_2 is from the symmetry group ($D_{\infty h}$). Dihydrogen can be detected in regions where the flux of ultraviolet photons is sufficiently screened to limit the dissociation of the molecule. H_2 is the main molecule that contributes to the mass of galaxies' dense gases and plays a fundamental role in astrophysics, particularly in the processes that regulate star formation and the evolution of galaxies. The physical–chemistry of the interstellar gases is initiated by the formation of H_2 on dust grains and it is dihydrogen that mainly contributes to the cooling of the astrophysical media via collisional processes. In the presence of radiation in the far UV range, H_2 is electronically excited and relaxes radiatively or non-radiatively to the fundamental electronic level, thus populating the high vibrational energy levels, which then emit fluorescence in the optical and infrared range. The electronic transitions of H_2 in UV cannot be detected from instruments based on the ground and require platforms above the earth's atmosphere because the latter is opaque to UV radiation. As H_2 is symmetric, the transitions are due to the very weak quadrupolar moment. In the case of the HD isotopologue, a dipole moment is present because the barycenter of negative charges does not coincide with that of the nuclei and, although very weak, it allows this species to be detected in the infrared. Moreover, the difference of nuclear masses is responsible for a breakdown of the electronic symmetry (g-u parity) in an inversion of electronic coordinates with respect to the geometric center of the nuclei. Interactions between the electronic states that have different symmetries are then possible and transitions forbidden with the H_2 or D_2 isotpologues are then possible.

The formulation of the Hamiltonian of a diatomic molecule is different if the origin of the reference frame connected to the molecule is placed at the nuclei's CM or if it is placed at the geometric center of the molecule. If we focus on the electronic spectra, it is more judicious to place the origin of the molecular reference frame at the geometric center. However, if our interest is on the vibration–rotation spectra when the molecule is in its fundamental electronic state, it is wiser to place the origin of the molecular reference frame at the nuclei's CM.

In a reference frame whose origin is at the geometric center of the diatomic molecule, the Hamiltonian is expressed as:

$$H_{eTVR} = T_{CM} + H_e + H_N + H_{pm} + H_{gu} \quad [1.13a]$$

with

$$T_{CM} = -\frac{\hbar^2}{2M}\nabla^2_{CM} \quad [1.13b]$$

$$H_e = \sum_{e=1}^{2}\left\{-\frac{\hbar^2}{2m_e}\nabla^2_e + V\left(\vec{r}_e, \vec{R}_N\right)\right\} \quad [1.13c]$$

$$H_N = -\frac{\hbar^2}{2m_N}\nabla^2_{R_N} \quad [1.13d]$$

$$H_{pm} = -\frac{\hbar^2}{8m_N}\sum_{e,e'=1}^{2}\vec{\nabla}_e\vec{\nabla}_{e'} \quad [1.13e]$$

$$H_{gu} = -\frac{\hbar^2}{2\mathrm{m}_\alpha}\vec{\nabla}_{R_N}\sum_{e=1}^{2}\vec{\nabla}_e\ , \quad [1.13f]$$

where $m_N = \frac{M_1 M_2}{M_1 + M_2}$ is the reduced mass of the nuclei with mass M_1 and M_2, and $\mathrm{m}_\alpha = \frac{M_1 M_2}{M_1 - M_2}$. With respect to the reference frame whose origin is the CM of the nuclei, an additional term H_{gu} is present and disappears when the nuclei have the same mass and the term H_{pm} connected to the mass polarization is divided by 4. In this frame, the term H_{gu} explicitly highlights the difference between the H_2 and HD isotopologues.

If we explicate the electrostatic interaction term, $\sum_{e=1}^{2} V\left(\vec{r}_e, \vec{R}_N\right)$, we can write that:

$$\sum_{e=1}^{2} V\left(\vec{r}_e, \vec{R}_N\right) = \frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_1 - \vec{r}_2\right|} + \frac{e^2}{4\pi\varepsilon_0\left|\vec{R}_1 - \vec{R}_2\right|} - \sum_{i=1}^{2}\sum_{k=1}^{2}\frac{e^2}{4\pi\varepsilon_0\left|\vec{R}_i - \vec{r}_k\right|} \quad [1.14]$$

which allows the electronic and nuclear Hamiltonians to be rearranged under the following form, by disregarding the terms H_{pm} and H_{gu}:

$$H = H_e + H_N + H_{eN} \tag{1.15a}$$

with

$$H_e = -\frac{\hbar^2}{2m_e}\nabla_e^2 + \frac{e^2}{4\pi\varepsilon_0 \left|\vec{r}_1 - \vec{r}_2\right|} \tag{1.15b}$$

$$H_N = -\frac{\hbar^2}{2m_N}\nabla_{R_N}^2 + \frac{e^2}{4\pi\varepsilon_0 \left|\vec{R}_1 - \vec{R}_2\right|} \tag{1.15c}$$

$$H_{eN} = -\sum_{i=1}^{2}\sum_{k=1}^{2}\frac{e^2}{4\pi\varepsilon_0 \left|\vec{R}_i - \vec{r}_k\right|} \tag{1.15d}$$

To determine the molecule's energy levels, the Schrödinger eigenvalues equation must be solved for the molecular system. This equation involves the degrees of freedom of the nuclei and the electrons composing the molecule and, in general, there are no simple analytic solutions. It is therefore necessary to proceed in steps and the successive steps to resolve it are hereafter outlined.

1.4.2. *BO approximation*

The BO approximation is based on the ratio of the masses of an electron and a nucleus (as the mass ratio is such that m_e/m_N <<1; for example, of the order of 0.0005 for the hydrogen atom). It is considered that electrons instantaneously follow the nucleus' movement as a result of their lighter mass. The nuclei ($\vec{R}_N$) are fixed and the following eigenvalues equation is solved:

$$H\Phi_k\left(\vec{r}_e,\vec{R}_N\right) = \left(H_e + H_{eN}\right)\Phi_k\left(\vec{r}_e,\vec{R}_N\right) = U_k\left(\vec{R}_N\right)\Phi_k\left(\vec{r}_e,\vec{R}_N\right) \tag{1.16}$$

where H is the Hamiltonian of the electronic system with $\vec{R}_N$ fixed.

We choose a solution in the form: $\Psi\left(\vec{r}_e,\vec{R}_N\right)=\sum_k \chi_k\left(\vec{R}_N\right)\Phi_k\left(\vec{r}_e,\vec{R}_N\right)$, to solve the equation:

$$\left(H_e + H_{eN} + H_N\right)\Psi\left(\vec{r}_e,\vec{R}_N\right)= E\Psi\left(\vec{r}_e,\vec{R}_N\right) \qquad [1.17]$$

Below, we will show how the BO approximation is applied to the simple diatomic molecule H_2. To simplify, we consider a solution in which the total wave function is a product of two functions only, $\Psi\left(\vec{r}_e,\vec{R}_N\right)=\Psi_e\Psi_N$. The calculations can easily be transposed to the function $\Psi\left(\vec{r}_e,\vec{R}_N\right)=\sum_k \chi_k\left(\vec{R}_N\right)\Phi_k\left(\vec{r}_e,\vec{R}_N\right)$.

For the system of electrons, we have:

$$\left(H_e + H_{eN}\right)\Psi_e = -\frac{\hbar^2}{2m_e}\nabla_e^2\Psi_e + \frac{e^2}{4\pi\varepsilon_0\left|\vec{r}_1-\vec{r}_2\right|}\Psi_e + H_{eN}\Psi_e = \varepsilon_e\Psi_e \qquad [1.18a]$$

where Ψ_e is a function of the electrons' coordinates and ε_e is an energy that is a constant for a given nuclear configuration. For another configuration, the solution Ψ_e,ε_e is different.

In this case, we can put equation [1.15c] in the following form:

$$H_N = -\frac{\hbar^2}{2m_N}\nabla_{R_N}^2 + \frac{e^2}{4\pi\varepsilon_0\left|\vec{R}_1-\vec{R}_2\right|} + \varepsilon_e\left(\left|\vec{R}_1-\vec{R}_2\right|\right) \qquad [1.18b]$$

where the second term on the right corresponds to the Coulomb repulsion of the nuclei and the third term corresponds to the average value of the attraction exerted by the electronic cloud on the nuclei.

For the full system of electrons and nuclei, we have:

$$\left(H_e + H_{eN} + H_N\right)\Psi_e\Psi_N = E\Psi_e\Psi_N \qquad [1.19a]$$

and, in the developed form, the expression is:

$$
\begin{aligned}
E\Psi_e\Psi_N &= -\Psi_N \frac{\hbar^2}{2m_e}\nabla_e^2\Psi_e + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\Psi_e\Psi_N + H_{eN}\Psi_e\Psi_N + \\
&-\Psi_e\frac{\hbar^2}{2m_N}\nabla_{R_N}^2\Psi_N + \frac{e^2}{4\pi\varepsilon_0\left|\vec{R}_1-\vec{R}_2\right|}\Psi_e\Psi_N \\
&-\Psi_N\frac{\hbar^2}{2m_N}\nabla_{R_N}^2\Psi_e + -2\frac{\hbar^2}{2m_N}\left(\frac{\partial\Psi_e}{\partial X_N}\frac{\partial\Psi_N}{\partial X_N}+\frac{\partial\Psi_e}{\partial Y_N}\frac{\partial\Psi_N}{\partial Y_N}+\frac{\partial\Psi_e}{\partial Z_N}\frac{\partial\Psi_N}{\partial Z_N}\right)
\end{aligned}
\quad [1.19b]
$$

The BO approximation consists of neglecting the variations of the electronic wave function (first and second derivatives) with respect to the nuclear coordinates, which corresponds to a negligible influence of the nuclei's movement on the electronic wave function. By taking the average of equation [1.19b] in the given electronic state, thereby:

$$
\begin{aligned}
E\langle\Psi_e|\Psi_e\rangle|\Psi_N\rangle &= \langle\Psi_e|\frac{-\hbar^2}{2m_e}\nabla_e^2 + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|} + H_{eN}|\Psi_e\rangle|\Psi_N\rangle + \\
&\langle\Psi_e|\Psi_e\rangle\left(-\frac{\hbar^2}{2m_N}\nabla_{R_N}^2 + \frac{e^2}{4\pi\varepsilon_0\left|\vec{R}_1-\vec{R}_2\right|}\right)|\Psi_N\rangle
\end{aligned}
\quad [1.20a]
$$

then the eigenvalues equation of the nuclear terms can be written as:

$$
\begin{aligned}
E_N^e|\Psi_N^e\rangle &= \left(-\frac{\hbar^2}{2m_N}\nabla_{R_N}^2 + \frac{e^2}{4\pi\varepsilon_0\left|\vec{R}_1-\vec{R}_2\right|} + \varepsilon_e\right)|\Psi_N^e\rangle \\
&= \left(-\frac{\hbar^2}{2m_N}\nabla_{R_N}^2 + V_N^e\right)|\Psi_N^e\rangle
\end{aligned}
\quad [1.20b]
$$

The nuclear wave functions only depend on the nuclear coordinates (vibration and rotation (section 2.4 of Chapter 2)) but are characterized by the electronic and nuclear quantum numbers. Similarly, the nuclear energy E_N^e and the potential V_N^e are evaluated with reference to the minimum of the potential curve of the electronic state considered (Figure 1.2). The molecule's total energy for a given electronic state is expressed as $E^e = V_N^{\min} + E_N^e$. In this expression, the first term only depends on the electronic quantum numbers (each state is labeled by the ordinate of the minimum of each potential curve and characterizes the molecule's electronic energy: Figure 1.2) and the second term depends on the electronic and nuclear quantum numbers.

1.4.3. *Adiabatic representation*

The total Hamiltonian is diagonal on the basis of exact eigenfunctions. An exact solution $\Psi_T^e\left(\vec{r}_e,\vec{R}_N\right)$ of the total Hamiltonian $H_T = H_e + H_{eN} + H_N$ must fulfill:

$$\left\langle \Psi_T^e \middle| H_T \middle| \Psi_T^{e'} \right\rangle = \delta_{ee'} E_T^e \qquad [1.21]$$

An exact solution can, in principle, be obtained under the form of an expansion on the basis of wave functions used in the BO approximation, such as:

$$\Psi_T^e\left(\vec{r}_e,\vec{R}_N\right) = \sum_{k,N_k} c_{e,N_k} \chi_{N_k}\left(\vec{R}_N\right)\Phi_k\left(\vec{r}_e,\vec{R}_N\right) \qquad [1.22]$$

The expansion coefficients are obtained by diagonalizing the total Hamiltonian matrix. The basis used is chosen such that the non-diagonal elements are as small as possible through the application of a unitary operation, such as with the Van Vleck method (section 2.2.6 of Chapter 2) [JOR 74, VAN 29]. When the BO approximation is valid, only a single expansion term subsists. When the non-diagonal elements are not negligible, only two expansion terms generally subsist.

1.4.4. *Diabatic representation*

When the non-diagonal elements are not negligible, particularly around a specific value of the internuclear distance (intersection of potential curves), the approximate wave functions used in the framework of the BO approximation introduce non-adiabatic coupling terms between the different electronic states of different symmetries. In general, the description of the molecular dynamics [LEF 04] of excited electronic states requires a description of the states beyond the BO approximation. In the adiabatic representation, the description is unique, but in the diabatic representation, this is not the case and there is an infinite number of possible representations. All the electronic states from any of these representations can form a complete basis set from the point of view of quantum mechanics. At the crossings, the adiabatic states can change dramatically, as a function of the nuclear coordinates. The derivatives with respect to the nuclei's displacements are very large and it can be very difficult to evaluate the non-adiabatic matrix terms. The non-diagonal elements $H_{ee'}$, which are larger than or of the same order of magnitude as the difference $H_{ee} - H_{e'e'}$ between the diagonal elements, are processed by diagonalizing the interaction block states. In the intersecting regions, the diabatic representation is more suitable. A processed example in the case of a diatomic molecule can be found, for example, in [LAN 75]. In a diatomic molecule, the adiabatic potential curves belonging to electronic states with the same symmetry generally do not cross.

1.5. Conclusion

This chapter introduces theoretical considerations focused on homonuclear and heteronuclear diatomic molecules. The full Hamiltonian operators in terms of all the degrees of freedom of a diatomic, both classical and the quantum ones, are recalled. The different scales of the different energies, eigenvalues of the Hamiltonian for the electronic, vibrational and rotational degrees of freedom, allow the total electronic and vibration–rotation state to be represented in a first approximation as a product of the Hamiltonian's eigenstates of each of the degrees of freedom within the framework of the BO approximation. From the symmetry properties of these eigenstates discussed, according to the nature of the molecule and its symmetry group, the interaction with the electromagnetic radiation that entails the matrix elements of an n-polar operator, leads to the spectral signature to be expected in the spectrum profile and to the selection rules. The symmetry of the fundamental electronic state and the type of diatomic molecule, whether homonuclear or heteronuclear, bring further modifications to the expected profile as a result of the alternation in intensity of the spectral lines when one takes the nucleus' spins into account. The case of the hydrogen molecule and its isotopologues is discussed to illustrate these considerations.

1.6. Appendix

A symmetry operation is an operation that brings an object into a new orientation which is equivalent to the old one. For a molecule, the symmetry operations with respect to its symmetry elements leave the molecule's equilibrium configuration invariant, meaning that the molecule coincides with itself. The possible symmetry elements of a molecule are the axes of rotation (proper axes), the inverse axes of rotations (improper axes), the planes of reflection symmetry and an inversion center. Five types of symmetry operations are depicted for a molecule:

– a rotation of an angle $2\pi/n$ around C_n, the rotation axis of the order n (if n = 1, this is the identity operation I); for a linear molecule, there is an infinite number of possible rotations of an angle φ around the internuclear axis z, which is labeled $C_z(\varphi)$ including the identity operation I;

– a rotation of an angle $2\pi/n$ around the axis C_n, followed by a reflection operation in a plane perpendicular to the axis which is termed S_n (improper rotation); for a linear molecule, there is an infinite number of improper rotations $S_z(\varphi)$ (rotation of an angle φ around the z axis followed from the reflection operation in a plane perpendicular to the axis passing through the center of the chemical bond), including the reflection operation with respect to the plane xy (rotation of an angle 0 around the z axis and an inversion S_2 or I with respect to the center of the chemical bond);

– for a symmetric linear molecule, there is an infinite number of rotations $C_t(\pi)$ of an angle π around the axes t perpendicular to z and passing through the origin;

– for a symmetric linear molecule, there is an infinite number of reflections σ_{zt} with respect to the planes zt containing the axis z and making any angle with the zx plane;

– the inversion with respect to the molecule's center of symmetry; for a symmetric linear molecule, the improper axis S_2 corresponds to the inversion with respect to the center of the chemical bond.

All the molecule's symmetry operations make up a symmetry point group in the mathematical sense [AMA 80a, CAM 88, LAN 75, WIL 80], and the symmetry elements may be grouped into categories. All of the symmetry operations O_j make up a group if the following conditions are fulfilled:

– the product $O_k = O_iO_j$ of two operations of the group is a member of the group;

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

– there is an operation I called identity such that $IO_i = O_iI = O_i$;

– for each operation O_i, an operation O_i^{-1} called the inverse of O_i, can be defined, such that $O_iO_i^{-1} = O_i^{-1}O_i = I$.

If, in addition, we have $O_iO_j = O_jO_i$ (commutativity), the group is said to be Abelian.

The symmetry operations can be represented by unitary square matrices in a basis constructed on the molecule's equilibrium configuration and the set of matrices associated with each symmetry operation constitutes a representation of the group. The matrices have the same multiplication table as the symmetry point group.

So, a representation of dimension n can be built on the basis $\{\Psi_1, \Psi_2, \Psi_3, ..., \Psi_n\}$, composed of the set of square n × n matrices each associated with an operation of the group. Three cases may arise in the way these matrices are formed:

– if all the representation matrices comprise two blocks, respectively, with p and n-p lines and columns aligned on the main diagonal line, such as:

$$\begin{pmatrix} \overbrace{\begin{pmatrix} * & * \\ * & * \end{pmatrix}}^{p} & \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \\ \begin{vmatrix} 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{vmatrix} & \underbrace{\begin{pmatrix} \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \\ \bullet & \bullet & \bullet \end{pmatrix}}_{n-p} \end{pmatrix} \quad [1.23]$$

The representation appears under a reduced form. The first p components of the basis transform into themselves and constitute the basis of a representation of dimension p; the n-p other components of the basis also transform into themselves and constitute the basis of a representation of dimension n-p.

– a representation that does not appear under a reduced form is said to be reducible if it is possible to find a new basis whose components are n independent linear combinations of $\{\Psi_1, \Psi_2, \Psi_3,..., \Psi_n\}$ by a similarity operation and such that the representation constructed on the new basis $\{\Psi'_1, \Psi'_2, \Psi'_3,..., \Psi'_n\}$ appears under a reduced form. It is possible that the two new representations of dimensions p and n-p are themselves reducible;

– if, by a similarity operation, the order of the matrices cannot be reduced, the representation is said to be irreducible.

The number of irreducible representations of a group is equal to the number of classes in the group. An irreducible representation can be defined by the trace of the matrix (sum of the diagonal elements) also called the character of each matrix of the representation. In one same category, the characters are identical. When the group is Abelian, meaning that the symmetry operations commute, each operation constitutes one class by itself.

A group can be represented by a table in two dimensions with the classes of the symmetry operations in abscissa (for each column) and the irreducible representations in ordinate (for each line). The elements of the table are the characters of the matrices associated with the operations. These tables are called "Tables of Characters", in which we add a column comprised of the coordinates X, Y or Z and the rotations, J_X, J_Y or J_Z and the products that form a basis for the irreducible representation connected to the line. In the reference text book [WIL 80], one can find more detailed explanations on group theory's application to molecules.

As an example, for the group $C_{\infty v}$ (Table 1.2), we have the two-dimensional representation with the basis $\{\Psi_{-m}, \Psi_{+m}\}$ for $m \geq 1$. In this representation, the matrices associated with the rotations $C_z(\varphi)$ are in the form $\begin{pmatrix} e^{-im\varphi} & 0 \\ 0 & e^{+im\varphi} \end{pmatrix}$. This representation is not in a reduced form as the matrices associated with the reflections σ_{zt} do not have the same structure.

This representation is irreducible and two-dimensional and is of the symmetry type $\Pi, \Delta, \Phi, \ldots$ following the value of $m = 1, 2, 3, \ldots$. The trace Tr of the square 2 × 2 matrix, representing the rotation symmetry operation of angle φ around the z axis and built on the basis $\{\Psi_{-1}, \Psi_{+1}\}$ allows the symmetry type of the doubly degenerate states to be defined. This trace is expressed as $Tr = 2 cos m\varphi$ and according to the value of $m = 1, 2, 3, ..$, the states $\{\Psi_{-1}, \Psi_{+1}\}$ are of the symmetry type $\Pi, \Delta, \Phi, \ldots$.