

Cavity ring-down spectroscopy of cold molecular samples

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Abstract

Cavity ring-down spectroscopy is a sensitive spectroscopic technique that allows to measure spectra of atoms, molecules or gas mixtures. This work presents the design and the results obtained with the first homemade CRDS experimental set-up in Université catholique de Louvain. Simulations of a part of the visible absorption spectrum of H_2O^{16} are presented and compared to experimental measurements. This comparison allows to assign rovibrational transitions starting from the ground vibrational state ($v_1 = 0, v_2 = 0, v_3 = 0$) and reaching rotational states belonging to the ($v_1 = 3, v_2 = 1, v_3 = 1$) vibrational states. This work presents the design and results obtained with a pulsed cavity ring-down spectrometer, the first built in UCL, working in the visible range (610 to 670 nm). This set-up has been characterised and presents a sensitivity of $\alpha_{\min} \approx 5.10^{-8} \text{ cm}^{-1}$ and a resolution of 0.4 cm^{-1} . Some preliminary simulations that pave the way to low temperature measurements are also detailed in this work.

List of symbols

ω	[rad/s]	Angular frequency
$\Delta\omega$	[rad/s]	Spectral width of a laser pulse
δ	[rad]	Phase lag due to a round-trip inside a laser cavity
α	[rad]	Phase lag induced by the reflection at a mirror
R	[/]	Reflectivity of the mirrors
T	[/]	Transmittivity of the mirrors
$\mathcal{L}$	[/]	Losses of the mirrors
$\mathcal{F}$	[/]	Finesse of an optical cavity
$\Delta\nu_{fsr}$	[Hz]	Free spectral range of an optical cavity
τ	[s]	Ring-down time
ν	[Hz]	Frequency
$\alpha(\nu)$	[cm ⁻¹]	Absorbtion coefficient at a given wavelength
$w(z)$	[mm]	Half-width of a Gaussian laser beam
$\mathcal{R}(z)$	[mm]	Radius of curvature of a Gaussian laser beam
z_R	[mm]	Rayleigh length
f_i	[m]	Focal length of a lens
λ	[nm]	Wavelength
$q(z)$	[/]	q-parameter of a gaussian laser beam
H	[W/(mK)]	Convection coefficient
λ_h	[W/(m ² K)]	Heat transfert coefficient
Γ	[1/s]	Emission rate
$\bar{\nu}$	[cm ⁻¹]	Wavenumber
I_a, I_b and I_c	[kg.m ²]	Principal inertia moments
A_e, B_e and C_e	[cm ⁻¹]	Rotational constants
J	[/]	Angular momentum quantum number
K_a	[/]	Projection of the rotational angular momentum on the a-axis
K_c	[/]	Projection of the rotational angular momentum on the c-axis
κ	[/]	Asymmetry parameter of an asymmetric top molecule
G	[/]	Group of the symmetry operators
$\mathcal{G}$	[/]	Group of the representation of the symmetry operators
$\chi(R)$	[/]	Character of a representation under a given operator
Γ^α	[/]	Representation of the element α

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Introduction

Spectroscopy is the science that studies the interactions between light and matter in the solid, liquid or gaseous form. This work only concerns the absorption of light by molecules in gaseous state. This absorption can be measured at several frequencies and ultimately an absorption spectrum can be obtained. Each line of the spectrum corresponds to a transition between two quantum states of the molecule; the intensity of a line depends on the probability of the corresponding transition, on the population and the degeneracy of the initial state.

The absorption can be characterised by the variation of intensity of light before (I_0) and after (I) the interaction with a molecule i of molar concentration n_i and absorption cross-section σ_i on a distance l , following the Beer-Lambert's law.

$$I = I_0 \exp(-\sigma_i n_i l)$$

Thanks to this relation and due to the unique structure of the energy levels of a molecule, the measurement of absorption spectra can therefore provide information about the composition and molar concentration of molecules inside a gas mixture. These pieces of information are interesting in various domains (biology, astrophysics, quantum physics, physical chemistry,...) of science explaining why spectroscopy is a widely used technique.

A domain that is deeply interested in the study of the absorption cross-section of different molecules is the one that is focussed on the involvement of greenhouse gases on the global radiative budget. Indeed, this knowledge as well as the one of the molar concentration of the molecules allow to determine the importance of different gases in the global warming ([1] and [2]). For example, the significance of O_2 and N_2 in the absorption of atmosphere can be studied [3].

Spectroscopy can also be used to study the aggregation of some molecules, for example the aggregation of the dioxygen under the form of a dimer produced by collisions between dioxygen molecules [4]. This complex has been formed in laboratory in order to study its absorption spectrum ([5] and [6]). Due to its presence in the atmosphere [7], the formation of this dimer has been deeply investigated in various atmospheric conditions ([8] and [9]) in order to determine its role on the global warming.

Various techniques aim at measuring absorption spectra of a given molecule or molecules mixture. The choice of the technique depends on the range of the electromagnetic spectrum that has to be investigated and on the resolution that has to be achieved; each technique possessing its own characteristics. However, all these methods have a common purpose : combining the highest resolution with the highest sensitivity and the quickest speed of measurement.

In the microwave range, the most frequently used technique is the chirped pulsed Fourier transform spectroscopy that can achieve relatively high sensitivity on a broadband frequency

range (12GHz). This technique is relatively fast and its high sensitivity is due to its ability to rapidly average several measurements [10].

In the visible (VIS) and near infrared (IR) ranges, the most common methods are the cavity ring-down spectroscopy (CRDS) and the cavity-enhanced absorption spectroscopy (CEAS). Both of these techniques are based on the trapping of light in an optical cavity composed of two mirrors of high reflectivity (up to 99.99%) in the range of interest. The limitation of these techniques is the limited frequency range of the high reflectivity of the cavity mirrors. These two techniques allow to achieve high sensitivity and high resolution, respectively up to $\alpha_{\min} = 5.10^{-12}\text{cm}^{-1}$ and $\Delta\bar{\nu} = 2, 16.10^{-5}\text{cm}^{-1}$ [11].

In the vacuum ultraviolet range (VUV), the techniques are less developed except for the recent development of a vacuum-ultraviolet frequency-modulation spectroscopic technique [12].

The purpose of this master thesis was to develop an experimental set-up that is able to measure the spectra of cold molecular samples with high sensitivity in the visible range. The interest of such a set-up is to bring to light the conditions of complexation for H_2O and O_2 molecules. Directly inspired from the work of [13] and [14], the experimental set-up was designed to proceed to low temperature CRDS measurements. The spectroscopic technique used to do it is the pulsed wave cavity ring-down spectroscopy [15]. The experimental spectra measured with the homemade instrument were compared to the results of partly homemade simulations.

This document is divided into three main chapters. Chapter 1 explains the cavity ring-down spectroscopy that is the experimental method used to study the molecular samples. This first chapter details the principles of the method thanks to its three main components. The understanding of this technique is essential to understand the third chapter of the document. This first chapter ends by a feasibility study. We evaluate on a computer, how to efficiently inject light in an optical cavity.

The simulations of the molecular absorption spectrum of the water molecule are presented in chapter 2. This second chapter contains a first section about the computation of the rotational Hamiltonian of the water molecule that is useful to determine its energy levels. The second section of this chapter details the simulation of the spectrum of the water molecule. The theoretical backgrounds used for both of these simulations are also detailed in this chapter.

Chapter 3 describes the experimental set-up designed during this master thesis as well as the LABVIEW routine developed to analyse the data obtained during the measurements. The analysis of these data is also detailed in this third chapter: the probed molecules are identified, the observed lines are assigned and the performances of the experimental set-up are characterised.

Cavity ring-down spectroscopy : Principles and applications

1.1 Description of the method

Cavity ring-down spectroscopy (CRDS) is a sensitive optical spectroscopy method used to perform absorption spectrum measurements. Its high sensitivity is due to the high interaction length between light and sample.

The path travelled by light during a cavity ring-down spectroscopy experiment can be divided into three spatially different parts. The first part of the set-up is the laser that is injected inside the cavity, the second one is the optical cavity and the third one is the output of the cavity. The first part of this chapter follows the same structure in order to describe the principle of this method. The sensitivity of the CRDS technique can still be improved by coupling it with an efficient injection of the light inside the cavity. This efficient injection of the light inside the cavity would increase the ratio of photons injected in the cavity and therefore the ratio of photons detected by the detector. This chapter ends with the description of a computer simulation that studies this effective injection of light inside the cavity.

1.2 Laser

The laser that is injected in the cavity, may be either pulsed [16] or continuous [17]. In this work, a pulsed laser was used. The main difference between a pulsed and a continuous laser is their spectral width. Indeed, if one considers a laser whose wavelength is 650 nm for example, the spectral width of the pulsed laser will be larger than the one of the continuous one. This can be explained thanks to Fourier analysis [18]. The temporal width Δt and the angular frequency width $\Delta\omega$ fulfil equation (1.1).

$$\Delta t \Delta\omega \leq \frac{1}{2} \quad (1.1)$$

The laser used in our set-up is pulsed at a frequency f of 30 Hz with pulses of a few nanoseconds duration. After consideration of equation (1.1) one can directly expect large differences in terms of resolution between a continuous and a pulsed laser. If one considers a coherence time of 1 s and a pulse of 10^{-9} s respectively for a continuous and a pulsed laser, one gets spectral widths of $\Delta\nu_{cont} \approx 1$ Hz and $\Delta\nu_{pulsed} \approx 1$ GHz respectively. These numbers are just mentioned to outline the expected difference in spectral resolution. In practice a lot of different factors influence the spectral width of a laser. This difference in the spectral widths is primordial in the difference between the continuous wave cavity ring-down spectroscopy and the pulsed one.

1.3 Optical cavity

This section is based on the development presented in [19]. The cavity considered in cavity ring-down spectroscopy is composed of two spherical mirrors a and b respectively for the one to the left and to the right of the optical cavity. It therefore acts as a Fabry-Perot resonator. The spectrum of such a cavity can be studied thanks to the principles of optics. The light beam injected by the laser inside the cavity will travel a large number of round trips inside the cavity which will result in an increase of the path of the light inside the cavity. Figure 1.1 represents a Fabry-Perot resonator of length L composed of two spherical mirrors a and b.

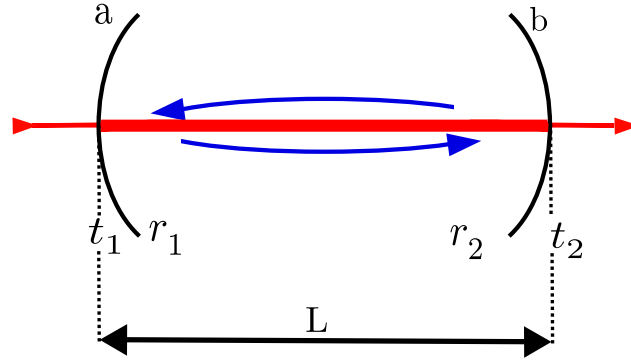


Figure 1.1: Representation of a Fabry-Perot resonator of length L composed of two spherical mirrors. The mirrors a and b have a given reflection and transmission coefficients respectively r_1 , t_1 and r_2 , t_2 .

Suppose an electromagnetic wave, emitted by the laser, whose magnitude of the electric field is U_0 . A fraction of this incident wave is transmitted into the resonator. The magnitude of this transmitted wave is $t_1 U_0$ where t_1 is the transmission coefficient of the entry mirror a. At each internal reflection, the intensity of the beam is multiplied by a factor r_1 (for the mirror a) or r_2 (for the mirror b). These factors are such that $r_1, r_2 < 1$.

Moreover, at each reflection at the mirror b, a fraction of the wave is transmitted. Further calculations allow to determine a global expression of the light transmitted by the Fabry-Perot resonator. This expression is given in equation (1.2).

$$U_{tr} = \frac{U_0 t_1 t_2}{1 - R \exp(i\delta)} \quad (1.2)$$

In equation (1.2), t_2 is the transmission coefficient of the second mirror b, considered as the output mirror of the cavity. R is the reflectivity of the mirrors (considered to be identical for the two mirrors) and is defined¹ by $R = |r_1|^2 = |r_2|^2$. The square of the modulus of the transmission coefficient will define the transmittivity T of the mirrors. By defining the losses at the mirrors by $\mathcal{L}$, it is possible to link these quantities by $R + \mathcal{L} + T = 1$. The term δ is the phase lag between two successive round trips, this is the combination of the phase lag induced by the reflections at the two mirrors and the one due to the second optical path difference. The component of the phase lag due to the round trips will depend on the angle of incidence of the beam. This dependence is given in equation (1.3). The angle of incidence is defined as the angle between the direction of propagation of the wave and the axis of the optical cell. The axis of the optical cell being defined by line normal to the centres of the mirrors.

¹This relation is not true for conductor mirrors that will induce a phase lag at the reflection. In our case, the mirrors were made of fused silica that is an insulating component.

$$\delta = k2d \cos(\theta) - \alpha \quad (1.3)$$

Where α is the phase lag induced by the reflection and θ is the incidence angle. The incidence angle of the laser is represented in Figure 1.2. If the laser is injected in the axis of the cavity, it will remain in this axis and if it is injected out of this axis, it will remain out of it. This second case corresponds to the off-axis cavity ring-down spectroscopy [20], a schematic representation of this method is shown in Figure 1.2. In the case of a null incident angle θ and if the wave inside the cavity is a stationary wave², the phase lag δ is an integer multiple of 2π . In order to ease the following calculations, one will consider that the laser beam is injected in the optical axis of the cavity.

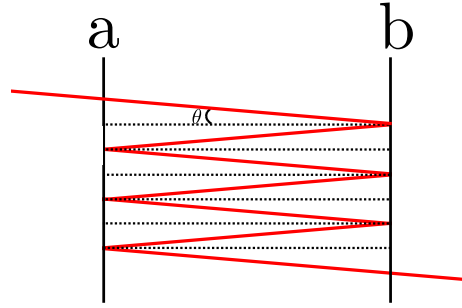


Figure 1.2: Representation of the off-axis cavity ring-down spectroscopy method in which the light beam is injected out of the axis of the cavity. The definition of the angle of incidence θ is also represented in this figure.

The intensity of an electromagnetic wave is proportional to the square of the modulus of the magnitude of its electric field. The transmitted intensity I_{tr} of an incident beam of intensity I_0 is given by equation (1.4). The first factor on the right member of this equation corresponds to the modulation of intensity due to the cavity whereas the second one represents the line shape of the lines of the spectrum of the cavity. This second term is an *Airy function*.

$$\frac{I_{tr}}{I_0} = \frac{|U_{tr}|^2}{|U_0|^2} = \overbrace{\left(\frac{|t_1 t_2|}{1 - R} \right)^2}^{\text{Amplitude modulation}} \overbrace{\frac{1}{1 + \frac{4R}{(1 - R)^2} \sin^2(\delta/2)}}^{\text{Airy function}} \quad (1.4)$$

This equation can be rewritten in terms of specific parameters of an optical cavity. One of these parameters is the finesse of the cavity $\mathcal{F}$. It is a non dimensional number that characterises how precisely the cavity is able to distinguish different frequencies. The definition of finesse is given by equation (1.5). One can see that it only depends on the reflectivity of the mirrors and that it does not depend on the incident light intensity or wavelength. It is therefore an intrinsic property of the cavity.

$$\mathcal{F} = \frac{\pi\sqrt{R}}{(1 - R)} \quad (1.5)$$

The finesse can also be expressed as a function of the difference of frequency between two successive lines of the spectrum of the cavity and the full width at half maximum of the lines

²It means that the length of the cavity is a entire number of times the wavelengths of the electromagnetic wave.

(FWHM). This relation is given by equation (1.6). In this equation, the difference of frequency between two successive lines is denoted by $\Delta\nu_{fsr}$ and it is called the free spectral range³ whereas the parameters that reflects the width of the lines is denoted by FWHM. Thanks to equation (1.6), the finesse can be understood as the energy contained inside of the cavity.

$$\mathcal{F} = \frac{\Delta\nu_{fsr}}{\text{FWHM}} \quad (1.6)$$

The expression of the transmitted intensity with respect to the incident intensity can be given by equation (1.7).

$$\frac{I_{tr}}{I_0} = \left(\frac{|t_1 t_2|}{1 - R} \right)^2 \frac{1}{1 + (4\mathcal{F}^2/\pi^2) \sin^2(\delta/2)} \quad (1.7)$$

Let us compute the values of the free spectral range and the finesse of the cavity for our case. The length of the cavity is $L = 560$ mm and the reflectivity of the mirrors is $R = 0.9999$. So one gets the results given by (1.8).

$$\begin{cases} \Delta\nu_{fsr} = \frac{c}{2L} = 0.26 \text{ GHz} \\ \mathcal{F} = \frac{\pi\sqrt{R}}{1 - R} = 31414 \end{cases} \quad (1.8)$$

Thanks to the values of the finesse and the free spectral range of the cavity, it is possible to compute the FWHM of the lines of the cavity. One finds $\text{FWHM} = 8.27$ kHz.

Figure 1.3 represents the spectrum of the cavity in the wavelength neighbourhood of 633 nm and the width of one line of the cavity spectrum. The quantities of interest are the separation distance between the different lines and the spectral width of the lines. The distance between the lines mainly depends on the length of the cavity whereas the width depends on the *finesse* $\mathcal{F}$ of the cavity so on the reflectivity of its mirrors.

The spectrum of the cavity allows to discuss the difference between a continuous and a pulsed laser used as incident laser in CRDS. In the case of the pulsed laser, it has been shown that the spectral width is of the order of the GHz. This means that a pulse of the laser will overlap with several lines of the cavity. It implies that there will always be light at the output of the cavity that can be usable for the CRDS measurement. In the case of continuous lasers, the spectral width of the emitted mode is much smaller, meaning that there is no guarantee that the spectra of the cavity and the one of the laser will overlap. In most cases, there will be no light at the detector. In order to address this problem, it is possible to mount the mirrors of the cavity on a piezoelectric crystal to tune the length of the cavity in order to overlap the laser and cavity spectra for any frequency of the continuous wave laser [17].

1.4 Intensity measured by the detector

A schematic representation of the signal detected by the detector in pulsed CRDS is shown in Figure 1.4. Two different parts can be distinguished in this signal, the first part, that is due to the pulse of the laser, is increasing whereas the second part, that is due to the absorption inside the cavity, is the decreasing one. This second part of the signal is called the ring-down part. The first part has a very small duration compared to the one of the ring-down part, nanoseconds compared to some microseconds. The part of the signal that is due to the pulse of the laser will

³Note that the free spectral range is defined on the frequency point of view and if the spectrum is given in wavelengths, one has to proceed to a change of variables

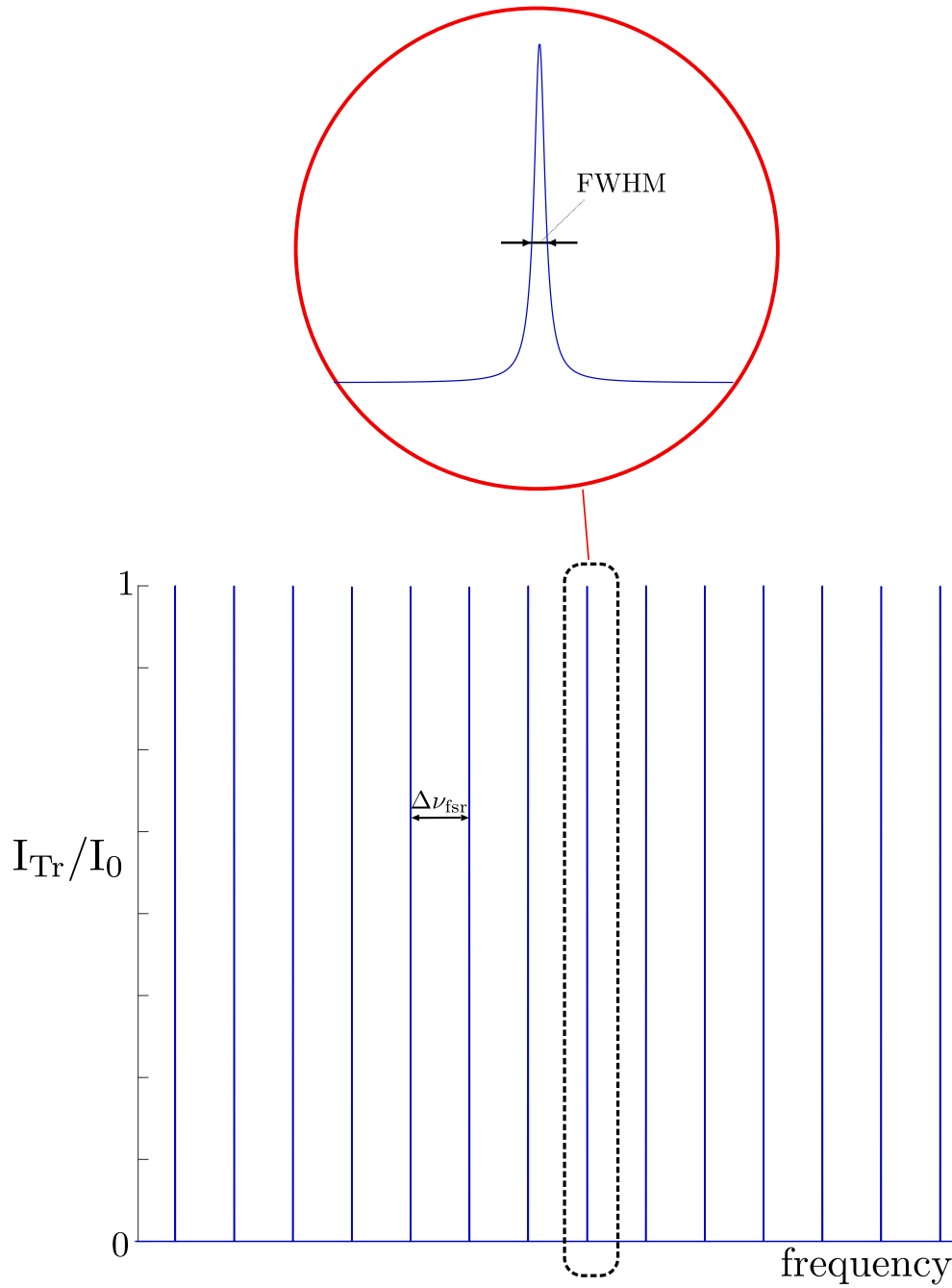


Figure 1.3: **Lower part:** Representation of the spectrum of a cavity whose length is $L = 560$ mm probed at a wavelength of $\lambda = 633$ nm. The free spectral range is also represented. **Upper part:** Representation of the line shape of one line of this spectrum along with the position of the full width at half maximum (FWHM) of this line.

not have a great importance in the measurement of the absorption spectrum, only the ring-down part will be considered.

The ring-down part can be mathematically expressed as an exponential decay. The absorption coefficient of the content of the cavity is linked to the characteristic time of this exponential decay. This exponential decay can be expressed by equation (1.9) where I_{Tr} is the intensity transmitted

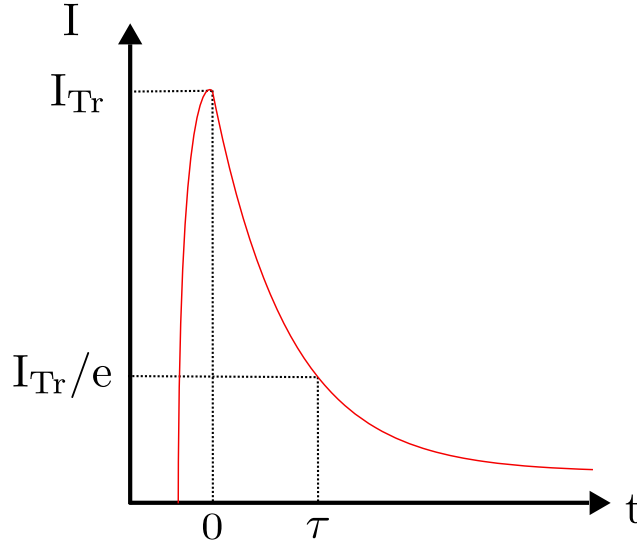


Figure 1.4: Signal obtained at the output of the cavity when a pulsed laser beam is injected inside it. Two parts can be distinguished, the first part of the signal is the one contained in the negative times. It corresponds to the pulse of the laser. The second part of the signal is the one contained in the positive times, it corresponds to the absorption of the cavity and its content.

by the cavity and τ the ring-down time. The ring-down time can be geometrically understood as the time at which the exponential decay has been reduced by a factor $\frac{1}{e} \approx 37\%$.

$$I(t) = I_{Tr} \exp\left(\frac{-t}{\tau}\right) \quad (1.9)$$

In order to obtain to absorption spectrum, it is necessary to first determine the value of the ring-down time of the empty cavity. This ring-down time only depends on the length of the cavity L and on the reflectivity of the mirrors R ; it is therefore an intrinsic property of the cavity. Equation (1.10) defines this ring-down time.

$$\tau_0 = \frac{L}{c(1-R)} \quad (1.10)$$

This cavity ring-down time is independent on the wavelength as long as the considered wavelength stays in the high reflectivity frequency range of the mirrors. If the considered wavelength is not in this range, the intrinsic ring-down time of the cavity will decrease.

When the cavity is not empty, the species that it contains will absorb the light at certain frequencies. The ring-down time of the non-empty cavity will therefore have a frequency dependence due to the absorption of all the species contained in the cavity. The expression of this ring-down time is given by equation (1.11).

$$\tau(\nu) = \frac{L}{c[(1-R) + \alpha(\nu)L]} \quad (1.11)$$

The term $\alpha(\nu)$, that contains the frequency dependence of the ring-down time, is the absorption coefficient of the species inside the cavity at the frequency ν . This ring-down time is smaller than the one of the empty cavity. This means that the more the gas mixture inside the cavity absorbs, the shorter will be the exponential decay. This expression of the ring-down involves the

absorption coefficient of the gas mixture contained in the cavity. With a small algebraic development, it is possible to express the absorption coefficient $\alpha(\nu)$ in terms of quantities that could be experimentally measured τ and τ_0 . This means that the analysis of the light intensity detected by the detector allows to obtain the absorption spectrum of the gas mixture since this one consists in the representation of this absorption coefficient with respect to the frequency.

Since the ring-down time and the exponential decay decrease when the species inside the cell are highly absorbing, the spectrum of highly absorbing species could be difficult to measure. In order to address this problem, it is necessary to optimise the number of photons injected in the cavity. In order to do it, it is important to increase, as far as possible, the ratio between the number of photons emitted by the laser and the one injected in the cavity. The next section of this chapter develops this problem.

1.5 Mode matching calculations

1.5.1 Introduction

We would like to proceed to molecular absorption spectroscopy in a sensitive manner by using laser and optical cavity. In order to have an intense signal at the output of the cavity and to reduce the losses in the system, it is required to match the mode of the laser beam, which is supposed to be Gaussian, with the one of the cavity. The mode of a laser beam is linked to the shape of its propagating ray and is characterised by two parameters. The first parameter, w , is the radius of the beam and the second parameter, $\mathcal{R}$, is the radius of curvature of the wavefront of the beam. Diverse optical devices can be used to shape the mode of the laser in order to geometrically match the mode of the cavity, this process is called mode matching. In our case two lenses of different focal lengths will be considered.

This section will firstly characterise the principal resonant mode of the cavity in order to find the required beam properties of the laser. Then two methods will be suggested for the mode matching problem. The first method will assume that the laser beam is non divergent and is based on the laws of the geometrical optics. The second method will assume that the laser beam has a Gaussian intensity profile and it therefore relies on the ABCD formalism and the q-parameter of a Gaussian beam to solve the mode matching problem. Finally, the results obtained with the second approach will be developed and discussed.

1.5.2 Beam properties of the cavity mode

The cavity considered here is composed of two spherical mirrors with the same radius of curvature, R_a separated by a distance L . The resonant mode of a cavity is a gaussian mode corresponding to a stationary wave inside the cavity. For each stationary wave, there are several resonant modes of different orders. The first order transverse electromagnetic mode of the cavity denoted by TEM_{00} is the less diverging one. For a given length of the cavity and a given radius of curvature of the mirrors, one can derive the mode of the first resonant mode of the cavity. Assuming a gaussian beam that travels along the z -axis with a wavenumber k and an electric field of amplitude U_0 ⁴, the evolution of its electric field along the z -axis can be described by the equation (1.12)[19].

$$U(x, y, z) = U_0 \left[\frac{w_0}{w(z)} \exp \left(\frac{-r^2}{w(z)^2} \right) \right] \exp \left[-i \left(kz - \arctan \left(\frac{z}{z_R} \right) \right) \right] \exp \left[-i \frac{kr^2}{2\mathcal{R}(z)} \right] \quad (1.12)$$

⁴We choose to only describe the electric part of the electromagnetic wave.

In this equation, the quantity w_0 is the beam waist of the resonant mode. It corresponds to the minimum half width of the beam inside the cavity. Since the laser beam is considered as a Gaussian beam, this half width is defined as the distance over which the intensity of the light has decreased of a factor $\frac{1}{e}$. For a cavity composed of two spherical mirrors that have the same radius of curvature, the beam waist is located at the centre of this cavity as illustrated in Figure 1.5. The quantity z_R is the Rayleigh length and it characterises the divergence of the gaussian beam. The term $w(z)$ can be expressed in terms of the beam waist w_0 and of the Rayleigh length z_R by

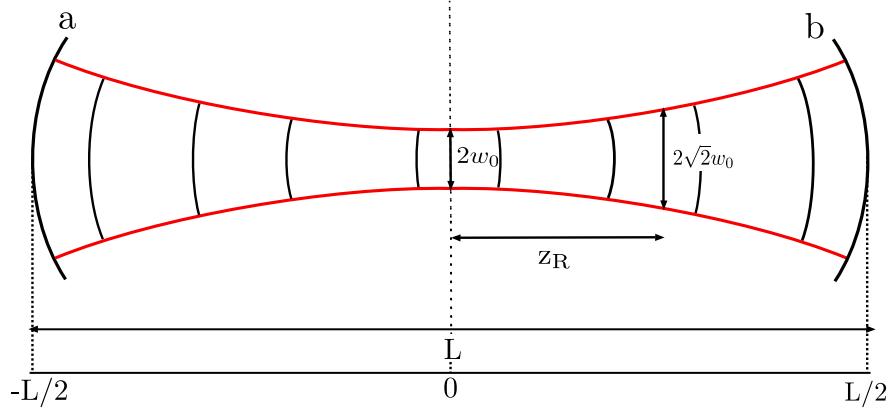


Figure 1.5: Representation of the first order transverse mode, TEM_{00} , of the optical cavity. The concepts of beam waist w_0 , Rayleigh length z_R are also illustrated in this figure.

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R}\right)^2} \quad (1.13)$$

whereas $\mathcal{R}(z)$, that is the radius of curvature of the Gaussian beam at position z can be expressed by

$$\mathcal{R}(z) = z \left[1 + \left(\frac{z_R}{z}\right)^2 \right] \quad (1.14)$$

The Rayleigh length, z_R that appears in both equations (1.13) and (1.14) is defined in equation (1.15). It represents the propagation distance required to increase the half width of the laser beam by a factor $\sqrt{2}$. This parameter is also linked to the divergence of the beam, indeed, the smaller is the Rayleigh length, the more divergent the beam is.

$$z_R = \frac{\pi w_0^2}{\lambda} \quad (1.15)$$

Let us now focus on the studied cavity represented in Figure 1.5. The parameters of the cavity are its length, L , the radius of curvature of the mirrors, R_a , and the wavelength of the resonant mode, λ . Moreover, in order to avoid losses, the radius of curvature of the gaussian beam must match with the one of the mirrors [21]. By referring to Figure 1.5, this involves that when $z = \pm \frac{L}{2}$ the radius of curvature of the beam must be given by equation (1.16). To obtain this equation, the radius of curvature and the position along the z axis have been replaced in equation (1.14).

$$R_a = \mathcal{R} = \frac{L}{2} + \frac{2z_R^2}{L} \quad (1.16)$$

An expression of z_R can thus be derived as a function of the cell parameters only⁵.

$$z_R = \sqrt{\frac{R_a L}{2} - \frac{L^2}{4}} \quad (1.17)$$

By injecting equation (1.17) into equation (1.13), it is possible to find the beam waist of the Gaussian beam inside the cavity and so to find the width of the beam at the a mirror. In the studied case, the parameters of the cavity are given in table 1.1.

L [mm]	R_a [mm]	λ [nm]
560	600	633

Table 1.1: Parameters of the homemade cavity, respectively its length, the radius of curvature of its mirrors and the wavelength of the beam injected in this cavity.

The Rayleigh length of our cavity is $z_R = 0.2993$ m. The waist size of TEM_{00} of the cavity is $w_0 = 245 \mu\text{m}$. It is possible to find the half width of the Gaussian beam at the left side of the cavity that is $w_{left} = 0.336$ mm. Now that all these parameters are known, it could be interesting to notice that the volume probed by the laser is on the order of 100 mm^3 .

1.5.3 Geometrical resolution

The solution to this mode matching problem involves two lenses of respective focal length f_1 and f_2 . Figure 1.6 represents the disposition of this solution. The laser that has to be introduced in the cavity is on the left of the figure. To the right of this laser, there are the two lenses respectively at distances d_1 and d_2 of the output of the laser. On the right side of the figure, there is the cavity already presented in more details in Figure 1.5. The distance between the output of the laser and the first mirror of the cavity (called a in Figure 1.5) is d_3 .

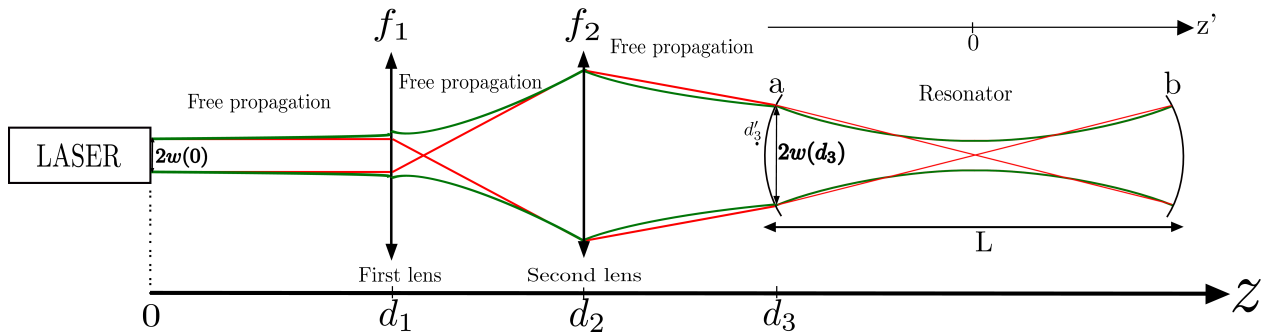


Figure 1.6: Representation of the mode matching problem. The light beam emitted by the laser has to be introduced inside the resonator thanks to two lenses of focal lengths f_1 and f_2 . The different distances and parameters are represented on the scheme. The red lines correspond to the geometrical resolution whereas the green ones represent the Gaussian resolution. The position of the d'_3 will be used in section 1.5.4.

A first intuitive way to solve this problem is based on the assumption that the distances of propagation of the beam will be small enough to neglect its divergence⁶. Divergence of the

⁵This means that, whatever the used wavelength is, the Rayleigh number of the cavity will not change.

⁶The light beam will thus be considered as a linear ray.

beam is characterised by the variation of $w(z)$ with respect to z . To evaluate the validity of this assumption the distance required to have an increase of 1% of the half width of the laser beam $w(z)$ has been computed. Assuming a He:Ne laser of wavelength $\lambda = 633$ nm and for which the width of the beam at the output of the laser is $2w = 2$ mm, the Rayleigh length, z_R , defined by the distance over which the width of the beam has been multiplied by a factor $\sqrt{2}$ compared to w_0 , can be determined by

$$z_R = \frac{\pi w_0^2}{\lambda} = 4,96 \text{ m.} \quad (1.18)$$

The evolution of the half width of the Gaussian beam depends on the Rayleigh length and is described by equation (1.13). The distance at which the beam has expanded of 1% can thus be computed and is $z = 0.70$ m. If the experiments are performed on small length this assumption is not too restrictive.

It is therefore assumed that the laser behaves as a ray and it is non-divergent as long as short distances are considered. A combination of two lenses will be used in order to proceed to mode matching, the principle described here is the same as the one involved in a telescope. These lenses have to reduce the width of the laser beam to the one of the first resonant mode of the cavity⁷. A rule of thumb for this type of mode matching is given by equation (1.19)[22].

$$\frac{f_2}{f_1} = \frac{w(d_3)}{w(0)} \quad (1.19)$$

Where f_1 and f_2 are respectively the focal length of the two lenses and $w(0)$ and $w(d_3)$ are respectively the waist size at the output of the laser and the one that is wanted at the entry of the cavity. This relation gives a way to find a correct couple of lenses for mode matching. Alongside their focal lengths, the distance between the lenses also has to be determined. Let us go back to the geometrical optics rules for a lens. If we suppose that the beam is collimated before the first lens, it can be said that it will converge to the focal point of this lens. If the focal point of the second lens coincides with the one of the first lens, then the beam will not be divergent after this second lens. This is represented in red in Figure 1.6.

A first glimpse of the solution consists thus in two lenses such that their focal lengths fulfil equation (1.19) and whose focal points are coinciding. However, this solution is based on assumptions that are too restrictive in the sense that they neglect the Gaussian behaviour of the laser mode as well as the divergence of the beam. In order to take them into account, the q-parameter of a Gaussian beam and the ABCD formalism have to be used.

1.5.4 Gaussian resolution

In this section, the problem will be solved using a formal approach based on the q-parameters of a Gaussian beam and on the ABCD formalism. However, equation (1.19) will be kept in mind because it allows to reduce the number of variables involved in the problem. We will thus assume that the focal lengths of the lenses are known. So, the unknowns that have to be determined are the positions of the lenses as well as the optical cavity with respect to the output of the laser.

As explained above, a Gaussian beam can be characterised by the radius of curvature of its wavefront and by the radius of the beam along its propagation axis. The q-parameter of a Gaussian beam is a complex parameter that gathers these two quantities to ease the study of the

⁷The width of this second beam is derived in section 1.5.2

influence of optical devices on the beam. This parameter is defined by equations (1.20) and (1.21)

$$q(z) = z + i z_R \quad (1.20)$$

$$\frac{1}{q(z)} = \frac{1}{\mathcal{R}(z)} - \frac{i\lambda}{\pi w(z)^2} \quad (1.21)$$

Where z is the position along the propagation axis, the origin of this axis is set at the waist of the laser, it is positive if the point is on the right side of the waist and negative otherwise (in this problem all the distances will be positive since they are located at the right side of the waist).

The q -parameter at the output of the laser is an unknown complex number. This complex number will vary with the laser cavity used. In this work, this q -parameter will be supposed to be purely imaginary. The q -parameter of the resonant beam just outside of the cavity will not be purely imaginary. Indeed, there is no guarantee that its radius of curvature is infinite. Henceforth, these two parameters will be referred to as q_{laser} and $q(d3')$ respectively for the initial q -parameter of the beam and for the q -parameter of the laser beam at the inner side of the a mirror.

The ABCD formalism is used to describe the effect of each optical device on a Gaussian beam and is based on the q -parameter. Each optical device possesses its own ABCD matrix, that represents its influence on the beam. The ones that will be used for this problem are the ones of a free propagation along a distance L in a medium of refractive index n , the one of a convex lens of focal length f and the one at the output of the resonator. This third element is characterised by its thickness t_e , the radius of curvature of the concave mirror R_a and the refractive index of the medium constituting the mirror n . These matrices are the ones given in Table 1.2.

Optical element	ABCD matrix
Free propagation	$\begin{bmatrix} 1 & L/n_1 \\ 0 & 1 \end{bmatrix}$
Lens	$\begin{bmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{bmatrix}$
One path through the cavity mirror	$\begin{bmatrix} 1 & 0 \\ 0 & n_2 \end{bmatrix} \cdot \begin{bmatrix} 1 & t_e \\ 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 1 & 0 \\ \frac{1-n}{R_a n} & \frac{1}{n} \end{bmatrix}$

Table 1.2: ABCD transfer matrices of the different optical elements involved in the solution of the mode matching problem.

If a beam of parameter q goes through an optical device described by the ABCD matrix $\begin{bmatrix} A & B \\ C & D \end{bmatrix}$ its new beam parameter q' is given by equation (1.22) (cfr Ref. [21]).

$$q' = \frac{Aq + B}{Cq + D} \quad (1.22)$$

Let us consider the propagation of the light beam from its emission by the laser until its injection in the optical cavity. This beam encounters five different elements, alternatively three

free propagations and two concave lenses. The ABCD matrices of these different elements are given in Table 1.2. As said before, the ratio between the focal lengths of the lenses is already known. All the distances defined in Figure 1.6 still have to be determined. The q-parameter of the beam at the mirror a of the cavity must match with the one from the first resonant mode of this cavity.

The ABCD matrix of a series of optical elements is the product of the matrices associated with each element. The matrix on the far right of the product corresponds to the first element encountered and the one on the far left is the last one. It is therefore possible to write the ABCD matrix for our optical system.

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix} = \overbrace{\begin{bmatrix} 1 & d_3 \\ 0 & 1 \end{bmatrix}}^{\text{Free propagation}} \overbrace{\begin{bmatrix} 1 & 0 \\ -1/f_2 & 1 \end{bmatrix}}^{\text{Second lens}} \overbrace{\begin{bmatrix} 1 & d_2 \\ 0 & 1 \end{bmatrix}}^{\text{Free propagation}} \overbrace{\begin{bmatrix} 1 & 0 \\ -1/f_1 & 1 \end{bmatrix}}^{\text{First lens}} \overbrace{\begin{bmatrix} 1 & d_1 \\ 0 & 1 \end{bmatrix}}^{\text{Free propagation}} \quad (1.23)$$

$$= \begin{bmatrix} 1 - \frac{d_2}{f_1} + \frac{d_2 d_3}{f_1 f_2} - \frac{d_3}{f_2} - \frac{d_3}{f_1} & d_1 + d_2 - \frac{d_1 d_2}{f_1} + d_3 - \frac{d_3 d_1}{f_1} + \frac{d_1 d_2 d_3}{f_1 f_2} - \frac{d_3}{f_2} (d_1 + d_2) \\ \frac{d_2}{f_1 f_2} - \frac{1}{f_1} - \frac{1}{f_2} & 1 - \frac{d_1}{f_1} + \frac{d_1 d_2}{f_1 f_2} - \frac{d_1}{f_2} - \frac{d_2}{f_2} \end{bmatrix} \quad (1.24)$$

$$= \begin{bmatrix} A_1 & A_2 \\ A_3 & A_4 \end{bmatrix} \quad (1.25)$$

The beam parameter of the beam coming from the laser can therefore be expressed as a function of the elements of this matrix. Equation (1.25) is introduced to simplify the expression. The four elements of the matrix which appears in equation (1.24) will be replaced by A_1 , A_2 , A_3 and A_4 . The q-parameter of the light beam at the entry of the cavity (that corresponds here to the mirror a) by

$$q_{\text{laser}} = \frac{A_1 q(0) + A_2}{A_3 q(0) + A_4} \quad (1.26)$$

The last step before performing mode matching is to define the q-parameter of the first resonant mode at the left of the mirror a ; this parameter is denoted by $q(d'_3)$, where d'_3 is the point located just before the resonator. This parameter can be characterised by the propagation of $q(d_3)$ through the matrix $ABCD_{\text{resonator}}$. We get the equation (1.27)

$$q(d'_3) = \frac{\left[1 + t_e \left(\frac{1-n}{Rn} \right) \right] q(d_3) + \frac{t_e}{n}}{\left[\frac{1-n}{Rn^2} \right] q(d_3) + \frac{1}{n^2}} \quad (1.27)$$

The condition of mode matching can then be written as

$$q_{\text{laser}} = q(d'_3) \quad (1.28)$$

These two q-parameters are complex numbers, which means that their real and imaginary part have to be equal to one another. These two conditions give rise to a system of two non-linear

equations with d_1 , d_2 and d_3 as unknowns. The system can be written

$$\begin{cases} \frac{A_2 A_4 - q_{\text{laser}}^2 A_1 A_3}{A_4^2 - A_3^2 |q_{\text{laser}}|^2} = \mathbb{R}(q_{d'_3}) \\ \frac{(A_1 A_4 - A_2 A_3) q_{\text{laser}}}{A_4^2 - A_3^2 |q_{\text{laser}}|^2} = \mathbb{I}(q_{d'_3}) \end{cases}$$

This system is numerically solved using the *fsolve* solver of MATLAB. This solver proceeds to resolution of non-linear systems using the *Levenberg-Marquardt* algorithm. The convergence criterion used to stop the iteration is a difference of 10^{-10} between the evaluation of the function between two successive iterations. The source code used to do it can be found in appendix C.1.

1.5.5 Results

To run the calculations of mode matching, the values of the different parameters were the length of the cavity, $L = 560$ mm, the radius of curvature of the mirrors inside the cavity, $R = 600$ mm, and the refractive index of the mirror, $n = 1.45$. The problem was solved thanks to a couple of lenses that verify the relation between the two focal lengths $f_1 = 1$ m and $f_2 = 0.336$ m. The results obtained are shown in the listings below.

Results numerically obtained

1		
2	Distances =	
3	0.708277535505684	1.496881329472574
	0.500530196243213	
4		
5		
6	fval = 1.0e-11 *	
7	0.214361861594625	0.441932601624728

The first line gives the distances in meters that allow to perform mode matching. The first distance is d_1 , the second d_2 and the third d_3 . The second line gives the difference of the real and imaginary part between q_{laser} at d'_3 and the q-parameter of the mode of the cavity at d'_3 . The calculation has converged since we have an error almost equal to zero within our numerical error on both the real and imaginary parts. The iteration has been stopped thanks to the convergence criterion resulting in the non-zero value of the function.

Figure 1.7 illustrates the evolution of the waist along the optical axis. Two different regimes are observed, this is why the optical system has been considered as two different parts. The first one is the combination of the lenses (located out of the optical cavity), we can attest that there is a waist between the two lenses. This waist is important because at a waist, the sign of the radius of curvature changes. The second part of this system is the cavity itself. There is a waist at the centre of the cavity, the mode shown in the cavity is the principal resonant mode. This figure shows that the mode matching was well performed.

The evolution of the radius of curvature is shown in Figure 1.8. Two different types of irregularities can be seen on this graph. The first one is a step in the radius of curvature combined

with a change of its sign (it corresponds to the two red dashed boxes in Figure 1.8). This step corresponds to the convex lenses used in this problem. Indeed, a convex lens will change the sign of the radius of curvature, meaning that the concavity of the wavefront will change too. The second type of irregularity is the exponential increase towards infinity. These irregularities are linked to the waists because at a waist the radius of curvature tends towards infinity and then changes its sign.

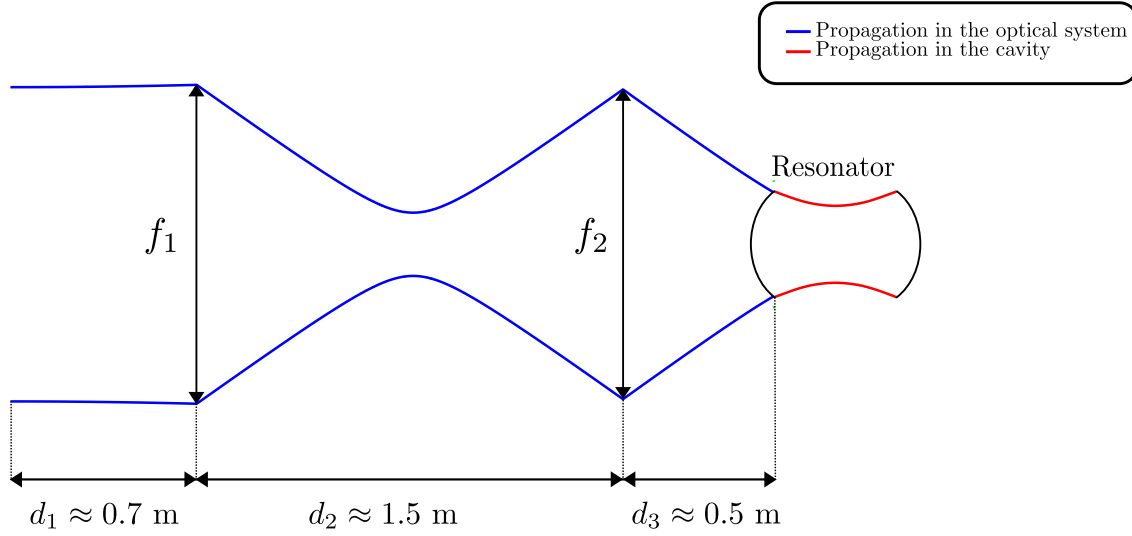


Figure 1.7: Evolution of the width of the beam along the optical axis.

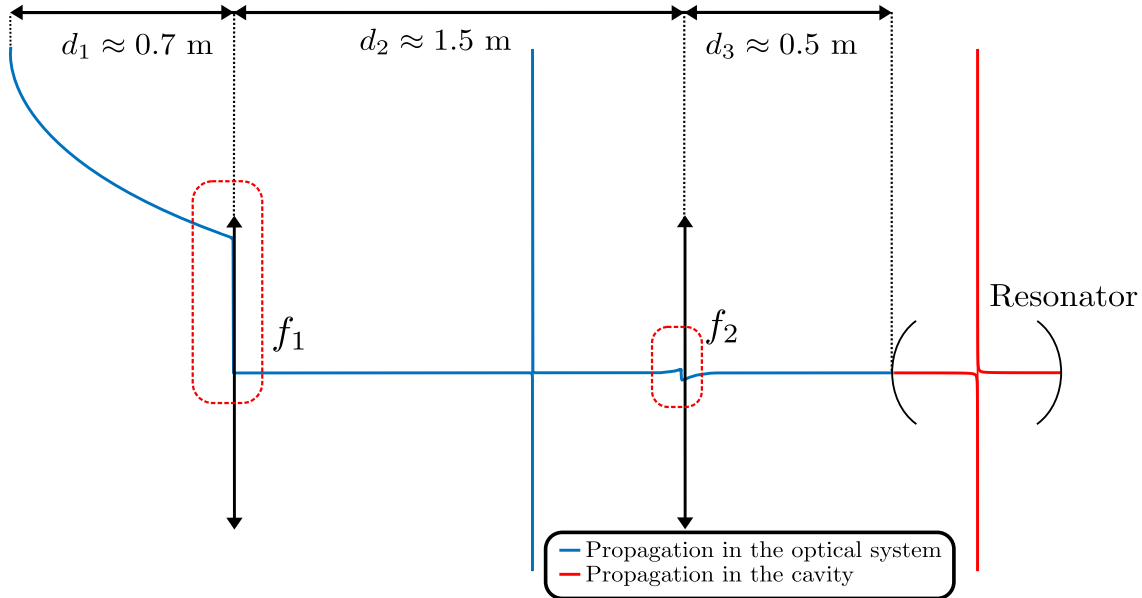


Figure 1.8: Evolution of the radius of curvature of the beam along the optical axis.

Absorption spectrum simulations

2.1 Introduction

This chapter describes the theoretical background required to perform and understand simulations of the absorption spectrum of the water molecule. The first part of this chapter is about the computation of the rotational energy levels of this molecule. This computation is based on the diagonalisation of the rigid rotor rotational Hamiltonian of H_2O . The second part of this chapter is about the simulation of the spectrum of the water molecule. This simulation is based on the symmetry selection rules that are also derived in this chapter.

2.2 Rotational Hamiltonian of the water molecule

2.2.1 Pure rotational case

Molecules, once considered as tops, can be classified in terms of their principal inertia moments I_a , I_b and I_c respectively defined along the inertial principal axis a -, b - and c . These inertia moments are defined such that $I_a \leq I_b \leq I_c$. Two different types of molecules will be considered in this work. The first one is the set of symmetric top molecules; these molecules are such that two of their principal inertia moments are equal. They can either be qualified of prolate if $I_a \leq I_b = I_c$, or oblate if $I_a = I_b \leq I_c$. The second type of tops is the set of the asymmetric top molecules; these molecules are such that all their principal inertia moments are different. Figure 2.1 represents these three different types of molecules. The prolate limit is represented by the CH_3Cl molecule, the oblate limit by the BF_3 molecule and the asymmetric top by the H_2O molecule. A correspondence between the xyz and the abc axis systems for each of these molecules is also represented in this figure.

The water molecule will be considered in its equilibrium configuration represented in Figure 2.1. It will therefore be considered as a rigid rotor molecule. This means that the lengths of the bonds between the atoms of the molecule are constant. The rotational Hamiltonian of the water molecule will consequently be a rigid rotor rotational Hamiltonian for an asymmetric molecule. Such an Hamiltonian is given by

$$\hat{H}_{\text{rot}} = \hbar^{-2} (A_e \hat{J}_a^2 + B_e \hat{J}_b^2 + C_e \hat{J}_c^2) \quad [\text{cm}^{-1}] \quad (2.1)$$

Where A_e , B_e and C_e , expressed in $[\text{cm}]^{-1}$, are the rotational constants defined by equation (2.2). The rotational constants are linked to the principal inertia moments and are thus different for each molecule. The operators $\hat{J}_a$, $\hat{J}_b$ and $\hat{J}_c$ are respectively the projection operators of the total angular momentum $\hat{\mathbf{J}}$ on the a -, b - and c -axis respectively.

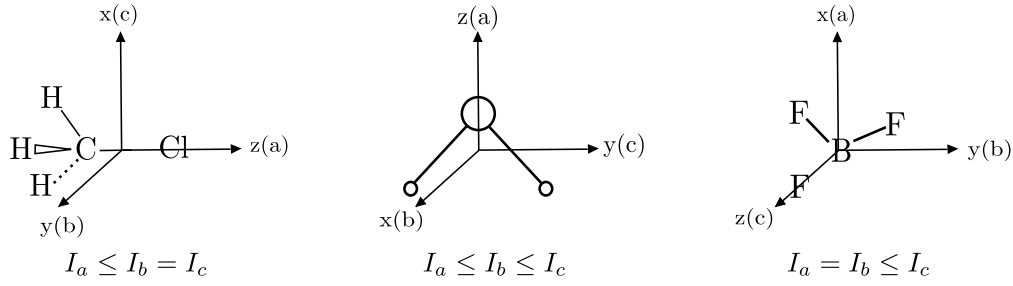


Figure 2.1: Representation of a prolate symmetric top (CH_3Cl), an asymmetric top (H_2O molecule) and an oblate symmetric top (BF_3) molecule. The correspondence between the abc and the xyz axis systems are given for each molecule.

$$\begin{cases} A_e = \frac{1}{2I_a} \\ B_e = \frac{1}{2I_b} \\ C_e = \frac{1}{2I_c} \end{cases} \quad (2.2)$$

The correspondence between the xyz axis system and the abc axis system used in this thesis, for the water molecule, is the so called type I convention : $abc = zxy$. With this convention, the Hamiltonian for the asymmetric top can be expressed in the xyz axis system by equation (2.3).

$$\hat{H}_{\text{rot}} = \hbar^{-2} \left(A_e \hat{J}_z^2 + B_e \hat{J}_x^2 + C_e \hat{J}_y^2 \right) \quad (2.3)$$

In order to ease the computation of the Hamiltonian matrix as well as the one of its eigenvalues, it is convenient to rewrite the equation (2.3) as follows.

$$\hat{H}_{\text{rot}} = \hbar^{-2} \left\{ \frac{B_e + C_e}{2} \hat{\mathbf{J}}^2 + \left[A_e - \frac{B_e + C_e}{2} \right] \hat{J}_z^2 + \left[\frac{B_e - C_e}{4} \right] \left[(\hat{J}_m^+)^2 + (\hat{J}_m^-)^2 \right] \right\} \quad (2.4)$$

Where $\hat{\mathbf{J}}$ is the total angular momentum operator, such that $\hat{\mathbf{J}}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2$, and $\hat{J}_m^+$ and $\hat{J}_m^-$ are respectively the ladder up and ladder down operators. These ladder operators are defined by equation (2.5).

$$\begin{cases} \hat{J}_m^+ = \hat{J}_x + i\hat{J}_y \\ \hat{J}_m^- = \hat{J}_x - i\hat{J}_y \end{cases} \rightarrow \begin{cases} (\hat{J}_m^+)^2 = \hat{J}_x^2 - \hat{J}_y^2 + 2i\hat{J}_x\hat{J}_y \\ (\hat{J}_m^-)^2 = \hat{J}_x^2 - \hat{J}_y^2 - 2i\hat{J}_x\hat{J}_y \end{cases} \quad (2.5)$$

With a small algebraic development, it can be proved that equations (2.3) and (2.4) are equivalent. This is done in equations (2.6) to (2.9).

$$\hat{H}_{\text{rot}} = \hbar^{-2} \left\{ \frac{B_e + C_e}{2} \hat{\mathbf{J}}^2 + \left[A_e - \frac{B_e + C_e}{2} \right] \hat{J}_z^2 + \left[\frac{B_e - C_e}{4} \right] \left[(\hat{J}_m^+)^2 + (\hat{J}_m^-)^2 \right] \right\} \quad (2.6)$$

$$\begin{aligned} &= \hbar^{-2} \left\{ \frac{B_e + C_e}{2} (\hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2) + \left[A_e - \frac{B_e + C_e}{2} \right] \hat{J}_z^2 + \left[\frac{B_e - C_e}{4} \right] \right. \\ &\quad \left. (\hat{J}_x^2 - \hat{J}_y^2 - 2i\hat{J}_x\hat{J}_y + \hat{J}_x^2 - \hat{J}_y^2 + 2i\hat{J}_x\hat{J}_y) \right\} \end{aligned} \quad (2.7)$$

$$= \hbar^{-2} \{ \hat{J}_x^2 B_e + \hat{J}_y^2 C_e + \hat{J}_z^2 A_e \} \quad (2.8)$$

$$= \hbar^{-2} \{ \hat{J}_b^2 B_e + \hat{J}_c^2 C_e + \hat{J}_a^2 A_e \} \quad (2.9)$$

Let us consider the time independent Schrödinger equation $\hat{H}_{\text{rot}} |\psi\rangle = E |\psi\rangle$ such that E is an eigenvalue of $\hat{H}_{\text{rot}}$ and $|\psi\rangle$ the eigenfunction corresponding to this eigenvalue. If this equation is projected on $\langle\psi|$, it becomes equation (2.10).

$$\langle\psi| \hat{H}_{\text{rot}} |\psi\rangle = E \langle\psi|\psi\rangle \quad (2.10)$$

Thanks to the property of orthogonality between eigenfunctions linked to different eigenvalues, the term on the right of equation (2.10) is a diagonal matrix with the eigenvalues of the Hamiltonian on its diagonal. This equation has to be expressed in terms of a basis set of wavefunctions. The basis set could have been intuitively chosen as a basis set composed of asymmetric top wavefunctions, however, such wavefunctions are not analytical. Another choice of basis set could be a basis set composed of symmetric top wavefunctions $|J, k, m\rangle$ being analytical. Nevertheless, there exists two type of symmetric tops, the oblate ones and the prolate ones. Two different basis set could thus be considered. In this master thesis, the chosen basis set will be the one of the symmetric tops in the prolate limit. The wavefunctions of this basis set are given by $|J, k_a, m\rangle$ with k_a the norm of the projection of the total angular momentum on the a -axis.

The term on the left of equation (2.10) is the matrix of the rigid rotor rotational Hamiltonian of the water molecule. Since the Hamiltonian can be expressed in terms of other operators, its matrix can also be expressed in terms of the matrices of these operators. The matrix elements of the operators $\hat{J}^2, \hat{J}_z^2, (\hat{J}_m^+)^2$ are therefore to be considered. The non zero matrix elements of these operators are given in [23].

$$\langle J, k, m | \hat{J}^2 | J, k, m \rangle = J(J+1) \hbar^2 \quad (2.11)$$

$$\langle J, k, m | \hat{J}_z^2 | J, k, m \rangle = k^2 \hbar^2 \quad (2.12)$$

$$\langle J, k-2, m | (\hat{J}_m^+)^2 | J, k, m \rangle = \sqrt{[J(J+1) - (k-1)(k-2)] [J(J+1) - k(k-1)]} \hbar^2 \quad (2.13)$$

$$\langle J, k+2, m | (\hat{J}_m^-)^2 | J, k, m \rangle = \sqrt{[J(J+1) - (k+1)(k+2)] [J(J+1) - k(k+1)]} \hbar^2 \quad (2.14)$$

The Hamiltonian matrix is thus block diagonal because no non zero element involves two different values of J . Each block corresponds to one value of J and has dimension $2J+1$. In these blocks, the non zero elements are located at positions represented by $\cdot \cdot$ in the matrices of Figure 2.2. The Hamiltonian matrix expressed in the basis set composed of the symmetric top molecules, $\hat{H}_{\text{sym}}$ is given by equation (2.15).

$$\langle J, k, m | \hat{H}_{\text{sym}} | J, k, m \rangle = B \langle\psi| \hat{H}_{\text{rot}} |\psi\rangle B^{-1} = BE \langle\psi|\psi\rangle B^{-1} \quad (2.15)$$

Where B is a unitary transformation matrix. A parallelism can be made between the term on the right of equation (2.15) and the diagonalisation of a matrix. Indeed, the matrix $E \langle\psi|\psi\rangle$ is diagonal and the B matrix is a unitary transformation. If this matrix on the left of this equation is numerically diagonalised, and if the diagonal and orthogonal matrices are identified, it will be possible to find the eigenenergies of the rigid rotor rotational Hamiltonian of the water molecule as well as the corresponding eigenfunctions.

2.2.2 Influence of the vibrations on the rotational Hamiltonian

However, the rotational Hamiltonian given in equation (2.4) is not totally correct since it does not take into account the distortions of the top due to vibrations. This effect, known as the centrifugal distortion, involves more rotational constants than A_e , B_e and C_e . The eigenvalues obtained thanks

$$\begin{array}{c}
|1_{-1}\rangle |1_0\rangle |1_1\rangle \\
|1_{-1}\rangle \begin{bmatrix} \ddots & 0 & \ddots \\ 0 & \ddots & 0 \\ \ddots & 0 & \ddots \end{bmatrix} \\
|1_0\rangle \\
|1_1\rangle
\end{array}
\begin{array}{c}
|2_{-2}\rangle |2_{-1}\rangle |2_0\rangle |2_1\rangle |2_2\rangle \\
|2_{-2}\rangle \begin{bmatrix} \ddots & 0 & \ddots & 0 & 0 \\ 0 & \ddots & 0 & \ddots & 0 \\ \ddots & 0 & \ddots & 0 & \ddots \\ 0 & \ddots & 0 & \ddots & 0 \\ 0 & 0 & \ddots & 0 & \ddots \end{bmatrix} \\
|2_{-1}\rangle \\
|2_0\rangle \\
|2_1\rangle \\
|2_2\rangle
\end{array}$$

Figure 2.2: Schematic representation of the rotational Hamiltonian matrices subblocks for $J=1$ (on the left) and $J=2$ (on the right). The non zero entries of the matrices are represented by the dots.

to the Hamiltonian that takes the centrifugal distortion into account are closer to the real values of the energy levels than the ones obtained with the purely rotational Hamiltonian. When the centrifugal distortion is taken into account, the non zero matrix elements of the Hamiltonian become longer as they involve lots of constants and higher order terms of J . They are given by (2.16) for the diagonal elements and (2.17) for the non diagonal elements [24].

$$\begin{aligned}
H_{k,k}^{\text{mat,dist}} &= \frac{B_e + C_e}{2} J(J+1) + \left(A_e - \frac{B_e + C_e}{2} \right) k^2 - \Delta_J J^2 (J+1)^2 - \Delta_{JK} J(J+1) k^2 \\
&\quad - \Delta_K k^4 + \Phi_J J^3 (J+1)^3 + \Phi_{JK} J^2 (J+1)^2 k^2 + \Phi_{KJ} J(J+1) k^4 + \Phi_K k^6
\end{aligned} \tag{2.16}$$

$$\begin{aligned}
H_{k\pm 2,k}^{\text{mat,dist}} &= \left\{ \frac{B_e - C_e}{4} - \delta_J J(J+1) - \frac{1}{2} \delta_K [(k\pm 2)^2 + k^2] + \Phi_J J^2 (J+1)^2 + \dots \right. \\
&\quad \left. \dots + \frac{1}{2} \Phi_{JK} J(J+1) [(k\pm 2)^2 + k^2] + \frac{\Phi_K}{2} [(k\pm 2)^4 + k^4] \right\} \dots \\
&\quad \dots \{ [J(J+A) - k(k\pm 1)] [J(J+1) - k(k\pm 1)(k\pm 2)] \}^{1/2}
\end{aligned} \tag{2.17}$$

The rotational constants involved in equations (2.16) and (2.17) as well as the power in J of the terms they are linked to are given in Table (2.1).

2.2.3 Identification of the energy levels

Once the energy levels are obtained by diagonalisation of the Hamiltonian matrix, it is necessary to identify them in terms of quantum numbers. Each of these levels can be labelled thanks to its total angular momentum J and the values of the projections of this total angular momentum on the a - and c - axis. These projections are respectively given by K_a and K_c . The aim of this section is to develop a systematic method to determine the label of each energy level.

- J is the total angular momentum. As mentioned before, the Hamiltonian matrix is block diagonal and each block corresponds to one value of J . Each energy level possesses its own eigenfunction that is expressed as a linear combination of the symmetric top wavefunctions that form the basis set. The coefficients of the linear combination are the elements of the column of the B matrix. The eigenfunction corresponding to a given eigenenergy only involves basis wavefunctions from a given block that corresponds to this value of J . This means that, to determine the value of J , it is sufficient to determine to which block the coefficients of the linear combination belong.

Constant	Power of J
$A_e = 835840.288$	2
$B_e = 435351.717$	2
$C_e = 278138.700$	2
$\Delta_J = 37.594$	4
$\Delta_{JK} = -172.9128$	4
$\Delta_K = 973.290$	4
$\delta_J = 15.210$	4
$\delta_K = 41.0502$	4
$\Phi_J = 1.565 \cdot 10^{-2}$	6
$\Phi_{JK} = -4.2081 \cdot 10^{-2}$	6
$\Phi_{KJ} = -5.095 \cdot 10^{-1}$	6
$\Phi_K = 3.733$	6

Table 2.1: Rotational constants of the A_1 $v=(0,0,0)$ ground state of H_2O expressed in [MHz]. The second column correspond to the order of the term that each constant multiplies.

• K_a is the norm of the projection of the total angular momentum on the a -axis.

The determination of K_a requires to consider the term in the linear combination of symmetric tops that has the highest absolute value (for a given column of the B matrix). This term or pair of terms will be the one of interest. For each subblock, there is a mapping of the vertical indexes with $-J, J+1, \dots, 0, \dots, J-1, J$. The value of K_a is the absolute value of the value of this mapping at the index corresponding to the largest absolute value of the coefficients involved in the linear combination of symmetric top wavefunctions.

• K_c is the projection of the total angular momentum on the c -axis. To determine its value, it is necessary to introduce the Wang transformation defined for $k = |K|$ and $s = 0$ or 1 by

$$\begin{cases} |JkMs\rangle = \frac{1}{\sqrt{2}} [|JkM\rangle + (-1)^s |J, -k, M\rangle] & \text{for } k \neq 0 \\ |J0M0\rangle = |J0M\rangle & \text{for } k = 0 \end{cases} \quad (2.18)$$

When Wang transformation (equation (2.18)) is applied to the molecular Hamiltonian, each block of the matrix will be split into four subblocks. These subblocks are labelled E^+ , E^- , O^+ and O^- . The letter E or O reflects the parity of k , respectively for an even (E) value and an odd (O) value of k . The sign $+$ or $-$ depends on the parity of s , if s is even, it is $+$ and $-$ otherwise. To determine it, it is necessary to have a look at Table 2.2. It is also necessary to introduce the symmetry species involved in the four different subblocks E^+ , E^- , O^+ and O^- . The symmetry species of these subblocks are summarised in Table 2.3. The irreducible representations present in this table are the ones that belong to the group D_2 . There exists an isomorphism between this group and the point group C_{2v} such that it is possible to correlate these irreducibles representations with the ones of C_{2v} . This correlation is given by equation (2.19).

$$\begin{cases} A \leftrightarrow A_1 \\ B_x \leftrightarrow A_2 \\ B_y \leftrightarrow B_2 \\ B_z \leftrightarrow B_1 \end{cases} \quad (2.19)$$

$K_a K_c$	Γ_{rot}
ee	A_1
eo	B_1
oe	B_2
oo	A_2

Table 2.2: Representation of the rotational wavefunction depending on the parity of K_a and K_c .

Subblock	k	s	J_{even}	J_{odd}
E^+	Even	0	A	B_z
E^-	Even	1	B_z	A
O^+	Odd	0	B_x	B_y
O^-	Odd	1	B_y	B_z

Table 2.3: Irreducible representations of the subblocks of the Hamiltonian matrix as a function of the parity of J , k and s .

Moreover, since K_a and K_c are respectively the projections of the total angular momentum J on the a -axis and on the c -axis. It can be said that $K_a + K_c = J$ or $J + 1$.

Thanks to all these pieces of information, an empirical formula can be derived for the value of K_c . This formula is given in equation (2.20).

$$K_c = J - K_a - \frac{(-1)^s - 1}{2} \quad (2.20)$$

Where $(-1)^s$ is equal to -1 if the terms involved in the linear combination of the Wang transformation are opposed in sign and $+1$ either.

This systematic method has been implemented with MATLAB and applied to the energy levels computed in 2.3 in order to label these levels.

2.3 Results and validation

The diagonalisation of the Hamiltonian matrix and the analysis of the obtained energy levels provide a set of energy levels with their labels. They are given in Table (2.4). This table summarises the energy levels obtained for $J = 0, 1, 2, 3$ by the simulation designed in this thesis.

It can be interesting to study the evolution of those energy levels while the considered molecule tends toward the oblate or the prolate limit. In order to do this, the value of the rotational constant B_e will be scanned between the ones of A_e (for the prolate limit) and C_e (for the oblate limit). The evolution of the symmetry of the molecule during this scan can be represented by the asymmetry parameter κ defined by equation (2.21).

$$\kappa = \frac{2B_e - (A_e - C_e)}{C_e - A_e} \quad (2.21)$$

This parameter takes values between -1 (in the prolate limit) and 1 (in the oblate limit). Figure 2.3 represents the evolution of the energy levels with the value of the asymmetry parameter. It can be noticed that the energy levels tend towards certain values that can be common to two or more different levels of the water molecule (the position of the water molecule along the axis of the asymmetry parameter κ is represented by the dashed line).

Energy [cm^{-1}]	J	K_a	K_c
0	0	0	0
23.79905	1	0	1
37.13691	1	1	1
42.37652	1	1	0
70.10105	2	0	2
79.50055	2	1	2
95.19515	2	1	1
134.90032	2	2	1
136.16644	2	2	0
136.77302	3	0	3
142.28317	3	1	3
173.39926	3	1	2
206.31568	3	2	2
212.18737	3	2	1
285.16004	3	3	1
2858.36124	3	3	0

Table 2.4: Energy levels numerically obtained by diagonalisation of the Hamiltonian matrix for the water molecule in its fundamental vibrational and electronic state.

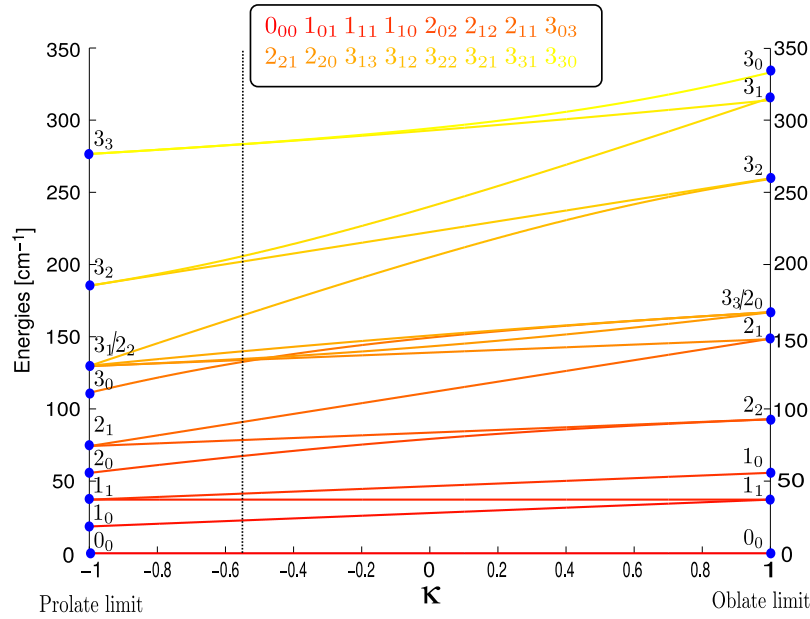


Figure 2.3: Evolution of the energy levels of the water molecule with the asymmetry parameter κ . The lines of different colors correspond to the different energy levels whose labels are given in the legend box. The blue dots are the result of an independent calculation of the prolate and oblate limits based on a symmetric top rotational wavefunction.

Figure 2.3 can be used to validate the labels that were attributed to the different energy levels. Indeed, it can be noticed that the limits of the levels obtained for the asymmetric top molecule tend toward to the values of some oblate or prolate energy levels computed for the symmetric top molecule. This figure therefore represents the correlation between the asymmetric top and

the prolate and oblate symmetric top models used for the water molecule. It however does not validate the value of the energy levels.

In order to quantify the precision of our code, it is necessary to compare the value of the energy levels that have been obtained by simulations with the ones of the supplementary information of Reference [25]. Figure 2.4 represents the relative error defined by $\left(E_{|J,K_a,K_c\rangle}^{\text{file}} - E_{|J,K_a,K_c\rangle}^{\text{computed}}\right) / E_{|J,K_a,K_c\rangle}^{\text{file}}$ for values of J up to three.

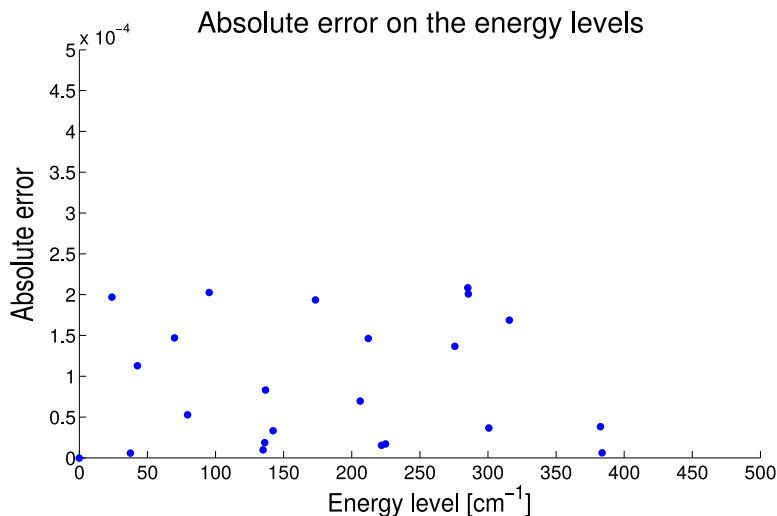


Figure 2.4: Absolute error done on the computation of the energy levels of the water molecule by comparison with the ones contained in the supplementary material of [25].

In Figure 2.4, it can be seen that the absolute error on the computed energy levels is smaller than 2.10^{-4} for all the energy levels considered. This means that it can be considered that the computed energy levels are correct and can thus be used in further calculations such as the calculations of the spectrum of the water molecule. However, it has not been done in this master thesis because the complete set of rotational constants was not found for other vibrational states than the fundamental one.

2.4 Computation of the spectrum

2.4.1 Introduction

This section determines the symmetry of the molecular wavefunction of the water molecule. Some basic notions of group theory and representation are reminded in appendix A.

2.4.2 Molecular symmetry

2.4.2.1 Definition of point group symmetry operations

A symmetry operation is an operation that leaves the skeleton of the molecule unchanged or that leaves it in an equivalent configuration. Five types of symmetry operations can be distinguished.

- *Identity* ($\hat{E}$): This operation does not change anything.

- *Rotation* ($\hat{C}_n$): This operation is a rotation of order n around a given axis. The order of rotation determines the rotation angle which is defined by $\alpha = \frac{2\pi}{n}$. If more than one rotation is executed, the operation is written $\hat{C}_n^k$ where k is the number of rotations executed.
- *Mirror plane* ($\hat{\sigma}_v$): This operation is a mirror plane symmetry operation. The index v defines the plane along which this symmetry operation is executed. This index can be v for a vertical plane, h for an horizontal one and d for a diagonal one.
- *Improper rotation* ($\hat{S}_n$): This operation is a combination of a rotation of order n defined as $\hat{C}_n$ followed by a reflection in the plane orthogonal to the rotation axis.
- *Inversion* ($\hat{i}$): This operation corresponds to a central symmetry and is characterised by its centre of symmetry O .

In the following, one will consider the group formed by the symmetry operations of a given molecule. This group is called the point group of this molecule because any operation of this group leaves, at least, one point unchanged. The determination of this point group will be helpful because it will define the character table corresponding to the studied molecule.

2.4.2.2 Application to the H₂O molecule

Now that the symmetry operations have been introduced, let us derive the symmetry group corresponding to the different rovibronic states of the water molecule. A water molecule is represented in Figure 2.5. This molecule presents two planes of symmetry σ_v and σ'_v respectively corresponding to the one in the plane of the molecule and the one orthogonal to this one. The molecule of H₂O also presents an axis of rotation C_2 .

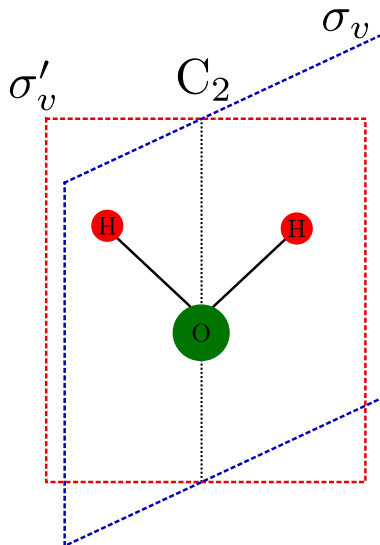


Figure 2.5: Symmetry operations of the point group of the H₂O molecule. The planes σ_v and σ'_v correspond to the reflection symmetry whereas the rotation axis C_2 corresponds to the rotation operation.

The group of the symmetry operations of the H₂O molecule contains thus four operations $\hat{E}$, $\hat{\sigma}_v$, $\hat{\sigma}'_v$ and $\hat{C}_2$. This group is called C_{2v} , its multiplication table is given in Table 2.5.

C_{2v}	$\hat{E}$	$\hat{\sigma}_v$	$\hat{\sigma}_{v'}$	$\hat{C}_2$
$\hat{E}$	$\hat{E}$	$\hat{\sigma}_v$	$\hat{\sigma}_{v'}$	$\hat{C}_2$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_{v'}$
$\hat{\sigma}_{v'}$	$\hat{\sigma}_{v'}$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}_v$
$\hat{C}_2$	$\hat{C}_2$	$\hat{\sigma}_{v'}$	$\hat{\sigma}_v$	$\hat{E}$

Table 2.5: Multiplication table of the C_{2v} point group.

The group C_{2v} possesses four equivalent classes and thus as many irreducible representations. The complete character table of this group is given in Table 2.6.

C_{2v}	E	C_2	$\sigma_{v'}$	$\sigma_{v''}$
$C_{2v}(M)$	E	(12)	E^*	$(12)^*$
Equiv. rot	R^0	R_b^π	R_c^π	R_a^π
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Table 2.6: Complete character table of H_2O and more generally of the group C_{2v}

This character table is said to be complete because it presents the point group and the others isomorphic groups. The first group is the point group of the molecule that has already been introduced in section 2.4.2.1. The second one is the group of molecular symmetry whose operations are either permutation of the nuclei ((12) for example represents the permutation of the 1 and 2 nuclei) or inversion of the coordinates of all the nuclei. The third group is the group of equivalent rotations, the definition of the symmetry operations that composes this group will be developed in section 2.4.3.3. The isomorphism between all these groups explains why the different operations are grouped in different rows.

The little and great orthogonality theorems (see appendix A) can easily be verified in this case. Indeed, it can be seen that the scalar product between any pair of rows or any pair of columns gives 0 as long as the two columns or rows considered are different from one another.

The last point that has to be introduced in order to find the allowed transitions between rovibronic states is the *vanishing integral rule*. This rule states that the quantum integral $\int \psi'^* \hat{O} \psi'' d\tau$ vanishes unless it contains the totally symmetric representation A_1 . This can be mathematically written as in equation (2.22). The term ψ' is the wavefunction of the final state whereas ψ'' is the wavefunction of the initial state. The term $\hat{O}$ is an operator that sends the initial state on the final one. In our case, this operator will be the dipolar moment operator $\hat{\mu}_A$.

$$\langle \psi' | \hat{O} | \psi'' \rangle \supset A_1 \quad (2.22)$$

In order to determine whether this integral contains or not A_1 it is necessary to consider the representations of ψ'^* , $\hat{O}$ and ψ'' . Let us call them respectively Γ' , Γ^μ and Γ'' . The representation of the integral will be determined by the direct product of these three representations whereas the characters of this representation under a given operation, R , will be obtained as the product of those of the three representations under the same operation. These results are summarised in equations (2.23) and (2.24).

$$\Gamma^{tot} = \Gamma' \otimes \Gamma^\mu \otimes \Gamma'' \quad (2.23)$$

$$\chi^{tot}(R) = \chi'(R) \chi^\mu(R) \chi''(R) \quad (2.24)$$

The symmetry of the representation Γ^μ is the same as Γ^* . Indeed, the electric dipole moment along a direction α is given by

$$M_\alpha = \sum_i e_i \alpha_i \quad (2.25)$$

With e_i being the charge of the particle i of coordinate α_i . This dipole moment is invariant to the inversion of two identical nuclei since they have the same charge. However, its character under the operations involving inversion is -1 . Therefore, the dipole moment is said to belong to the antisymmetric representation Γ^* which is the A_2 representation in the $C_{2v}(M)$ symmetry group.

2.4.3 Symmetry of the wavefunctions of the water molecule

Let us now consider the molecular wavefunctions of the H_2O molecule. If the degrees of freedom are decoupled, these wavefunctions can be considered as a product of rotational (rot), electronic (elec), vibrational (vib), nuclear spin (nspin) and electronic spin (espin) wavefunctions. The total wavefunction of the H_2O molecule can therefore be written

$$\psi_{\text{molec}} = \psi_{\text{elec}} \psi_{\text{rot}} \psi_{\text{vib}} \psi_{\text{espin}} \psi_{\text{nspin}} \quad (2.26)$$

Where ψ_{molec} is the total molecular wavefunction. In the case of the water molecule in its fundamental electronic state, the electronic spin is equal to 0 and the corresponding wavefunction is totally symmetric. Only four components of the molecular wavefunction need to be considered ψ_{elec} , ψ_{rot} , ψ_{vib} and ψ_{nspin} . The molecular wavefunction is thus a product of four wavefunctions. The wavefunction related to the electrons, ψ_{elec} , contains the information about the distribution of the electrons of the molecules inside the molecular orbitals. The second wavefunction, ψ_{rot} , contains the information about the rotational state of the molecule whereas the third one, ψ_{vib} contains the information about the vibrational state of the molecule. The last wavefunction considered, ψ_{nspin} contains the information about the spin of the nuclei contained in the molecule.

The absorption spectra that will be simulated here involve wavelength in the visible range. The energy in this range will not be high enough to create excited electronic states. This means that the water molecule will stay in its electronic fundamental state. Let us now derive the symmetry of these different wavefunctions.

2.4.3.1 Symmetry of the electronic wavefunctions ψ_{elec}

In order to determine the symmetry of the molecular electronic wavefunctions of the water molecule it is necessary to understand how these wavefunctions are built.

The electronic wavefunction of a given molecule can be written as a sum of single configuration wavefunctions ϕ_{det} (cfr equation 2.27).

$$\psi_{\text{elec}} = \sum_i c_i \phi_{\text{det}}^i \quad (2.27)$$

The function that is the sum of different functions of different symmetries has the symmetries of these different functions. This means that the symmetry of the electronic wavefunction is a combination of those of the single configuration wavefunctions.

Each of these single configuration wavefunctions is a product of molecular orbital wavefunctions defined by $\phi_{\text{MO},i}(r_j)$. The term r_j represents the positions of all the electrons of the molecular orbital. Each of these molecular orbital wavefunctions is a linear combination of atomic orbital wavefunctions $\phi_{\text{AO},i}$ of the atoms contained in the molecule. The symmetry of a given molecular

orbital wavefunction depends on those of the atomic orbital wavefunctions involved in its linear combination.

The atomic orbitals used for this combination are the orbitals of the constituting atoms. One thus has $1s(O)$, $2s(O)$, $2p_x(O)$, $2p_y(O)$, $2p_z(O)$, $1s(H_1)$ and $1s(H_2)$ respectively corresponding to the orbitals of the oxygen and hydrogen atoms.

In order to determine the symmetry of these atomic orbitals, it is necessary to study their transformation under the symmetry operations of the point group of the molecule. The comparison between the behaviour of these orbitals and the character table of the water molecule allows to determine the symmetry of each of these orbitals. From this atomic orbitals, it is possible to define the symmetry adapted combinations of atomic orbitals that are irreducible:

$$A_1: 1s(O), 2s(O), 2p_x(O), \frac{1}{\sqrt{2}} [1s(H_1) + 1s(H_2)]$$

$$B_1: 2p_y(O)$$

$$B_2: 2p_z(O), \frac{1}{\sqrt{2}} [1s(H_2) - 1s(H_1)]$$

The molecular orbitals being defined by linear combination of atomic orbitals, it is possible to determine the symmetry of these molecular orbitals on the basis of their constituting atomic orbitals. The molecular orbitals and their symmetry are given in Table 2.7 that has been obtained thanks to Ref. [23].

Molecular orbital	Linear combination	Symmetry
$1(a_1)$	$1s(O)$	A_1
$2(a_1)$	$\frac{1}{\sqrt{2}} \left\{ 2s(O) + \frac{1}{\sqrt{2}} [1s(H_2) + 1s(H_1)] \right\}$	A_1
$1(b_2)$	$\frac{1}{\sqrt{2}} \left\{ 2p_z(O) + \frac{1}{\sqrt{2}} [1s(H_2) - 1s(H_1)] \right\}$	B_2
$3(a_1)$	$\frac{1}{\sqrt{2}} \left\{ 2p_x(O) + \frac{1}{\sqrt{2}} [1s(H_2) + 1s(H_1)] \right\}$	A_1
$1(b_1)$	$2p_y(O)$	B_1

Table 2.7: Molecular orbitals of the water molecule and their symmetry.

The molecular orbitals given in Table 2.7 are the bonding orbitals. Each of these orbitals possesses an antibonding orbitals of the same symmetry. These antibonding orbitals are referred to $1(a_1^*)$, $2(a_1^*)$, $1(b_2^*)$, $3(a_1^*)$ and $1(b_1^*)$.

The next step consists in the determination of the symmetry of the single configuration wavefunctions. Since they are a product of molecular orbitals, their symmetry is defined as the direct product of the symmetries of the different molecular orbitals. The symmetry of a single configuration wavefunctions is therefore given by

$$(A_1)^2 \otimes (A_1)^2 \otimes (B_2)^2 \otimes (A_1)^2 \otimes (B_1)^2 = A_1 \quad (2.28)$$

Each single configuration wavefunction belongs to the totally symmetric representation A_1 . Since the molecular electronic wavefunction is a linear combination of such wavefunctions, one

can say that it also belongs to the totally symmetric representation A_1 . One can consequently write

$$\psi_{\text{elec}} \in A_1 \quad (2.29)$$

2.4.3.2 Symmetry of the vibrational wavefunctions

The determination of the symmetry of the vibrational wavefunctions involves to choose a basis set for the Cartesian displacement coordinates in the molecule field axis. Since there are three atoms, there will be nine such coordinates because, for each atom, one will define a Δx_i , Δy_i and on Δz_i corresponding to the displacement along the three axis of the molecule field axis; these displacements are represented in Figure 2.6. The study of the evolution of these Cartesian displacement coordinates with the symmetry operations of the molecule point group will allow to determine the representation of these $3N$ degrees of freedom (with N the number of atoms in the molecule).

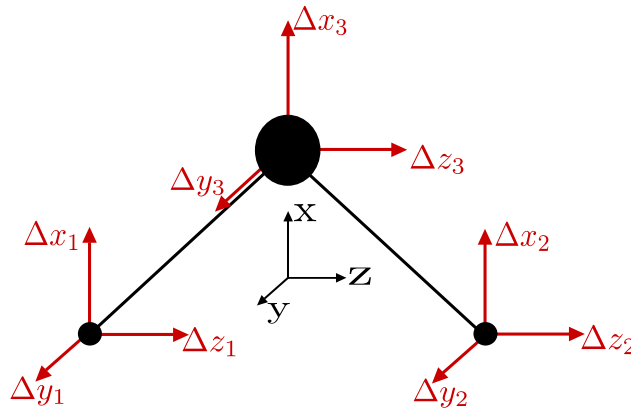


Figure 2.6: Representation of the cartesian displacements of the different atoms of the H_2O molecule.

Evolution of the Cartesian coordinates with $\hat{E}$

This operation is the one that leaves the molecule unchanged, one can thus write the following relation.

$$\begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} = \underbrace{D[\hat{E}]}_{\mathbb{1}_{(9 \times 9)}} \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} \quad (2.30)$$

The vectors correspond to the vectors of the Cartesian displacement coordinates whereas $\mathbb{1}_{(9 \times 9)}$ is an identity matrix of size 9×9 because it is the representation of the neutral element of the group. The character of this representation under the identity operation is therefore 9.

Evolution of the Cartesian displacement coordinates with $\hat{C}_2$

This operation is a rotation of angle π around the x-axis. If one considers that the axis system remains unchanged, one can write relation (2.31).

$$\begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} = \underbrace{\begin{bmatrix} 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}}_{D[\hat{C}_2]} \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} \quad (2.31)$$

The character of this representation for the $\hat{C}_2$ operation is thus -1.

Evolution of the Cartesian displacement coordinates with $\hat{\sigma}_v$

This operation is a mirror plane in the xz-plane. If one considers that the axis system remains unchanged, one can write relation (2.32).

$$\begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} = \underbrace{\begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}}_{D[\hat{\sigma}_v]} \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} \quad (2.32)$$

The character of this representation for the $\hat{\sigma}_v$ operation is 3.

Evolution of the Cartesian displacement coordinates with $\hat{\sigma}_{v'}$

This operation is a mirror plane in the xy-plane. If one considers that the axis system remains unchanged, one can write relation (2.33).

$$\begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} = \underbrace{\begin{bmatrix} 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}}_{D[\hat{\sigma}_{v'}]} \begin{bmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \\ \Delta y_1 \\ \Delta y_2 \\ \Delta y_3 \\ \Delta z_1 \\ \Delta z_2 \\ \Delta z_3 \end{bmatrix} \quad (2.33)$$

The character of this representation for the $\hat{\sigma}_{v'}$ operation is thus 1.

To summarise, the following characters are obtained

$$\chi_{\text{car}} [\hat{E}] = 9 \quad \chi_{\text{car}} [\hat{C}_2] = -1 \quad \chi_{\text{car}} [\hat{\sigma}_v] = 3 \quad \chi_{\text{car}} [\hat{\sigma}_{v'}] = 1 \quad (2.34)$$

These Cartesian displacement coordinates generate the representation Γ_{car} . However, these coordinates are not independent because they are linked to one another by two types of relations. The first one, called the center of mass condition, states that the centre of mass of a vibrating molecule does not move. The second one, called the Eckart condition, derives from the minimisation of the vibrational angular momentum of the molecule, in order to minimise ro-vibrational coupling.

These conditions can be written as in equations (2.35) and (2.36) respectively.

$$\begin{cases} T_x = \sum_i m_i \Delta x_i = 0 \\ T_y = \sum_i m_i \Delta y_i = 0 \\ T_z = \sum_i m_i \Delta z_i = 0 \end{cases} \quad (2.35) \quad \begin{cases} R_x = \sum_i m_i (y_i \Delta z_i - z_i \Delta y_i) = 0 \\ R_y = \sum_i m_i (z_i \Delta x_i - x_i \Delta z_i) = 0 \\ R_z = \sum_i m_i (x_i \Delta y_i - y_i \Delta x_i) = 0 \end{cases} \quad (2.36)$$

The representation of these relations is called $\Gamma_{\text{TR}} \oplus \Gamma_{\text{Rot}}$. It can be said that $\Gamma_{\text{car}} = \Gamma_{\text{Tr}} \oplus \Gamma_{\text{Rot}} \oplus \Gamma_{\text{Q}}$ where Γ_{Q} is the representation of the normal coordinates that will determine the symmetry of the vibrational wavefunction considered and Γ_{rot} is the representation associated to the Euler angles.

By proceeding as in equations (2.30) to (2.33) on T_x , T_y , T_z , R_x , R_y and R_z , it is possible to determine the characters of this representation under the symmetry operations of the point group of the water molecule.

$$\chi_{\text{TR} \oplus \text{Rot}} [\hat{E}] = 6 \quad \chi_{\text{TR} \oplus \text{Rot}} [\hat{C}_2] = 2 \quad \chi_{\text{TR} \oplus \text{Rot}} [\hat{\sigma}_v] = 0 \quad \chi_{\text{TR} \oplus \text{Rot}} [\hat{\sigma}_{v'}] = 0 \quad (2.37)$$

Hence the characters of the representation Γ_{Q} can be determined by substratcting (2.34) from (2.37).

$$\chi_{\text{Q}} [\hat{E}] = 3 \quad \chi_{\text{Q}} [\hat{C}_2] = 1 \quad \chi_{\text{Q}} [\hat{\sigma}_v] = 3 \quad \chi_{\text{Q}} [\hat{\sigma}_{v'}] = 1 \quad (2.38)$$

The decomposition of Γ_{Q} into irreducible representations allows to discuss the symmetry of the vibrational wavefunctions of H_2O : $\Gamma_{\text{Q}} = 2\mathbf{A}_1 \oplus \mathbf{B}_2$ ¹. It could now be interesting to consider the three vibrational modes of the water molecule. According to the Herzberg notation, they are defined as shown in Figure 2.7. The two representations $\mathbf{A}_1$ therefore correspond to the symmetric stretch and the bend (that are symmetric modes) whereas the representation $\mathbf{B}_2$ corresponds to the asymmetric stretch. The symmetry of the vibrational wavefunction of a given mode $\nu_1\nu_2\nu_3$ will thus depends on the parity of ν_3 . If ν_3 is even $\Gamma_{\nu_1\nu_2(\nu_3)^{2n}} = \mathbf{A}_1$ whereas if it is odd $\Gamma_{\nu_1\nu_2(\nu_3)^{2n+1}} = \mathbf{B}_2$ with $n \in \mathbb{R}$.

2.4.3.3 Symmetry of the rotational wavefunctions

The rotational wavefunctions of an asymmetric top molecule will be expressed in terms of wavefunctions of a certain basis set. The basis set of the asymmetric top wavefunctions cannot be chosen because these wavefunctions are not analytical. Two types of basis set of wavefunctions can be chosen corresponding to the prolate and oblate limits respectively. The asymmetric top wavefunction expressed in these basis will be given by

$$\psi_{\text{rot}} = \sum_k c_k |J, k, m\rangle \quad (2.39)$$

¹This decomposition is done using the small and great orthogonality theorems described in appendix A

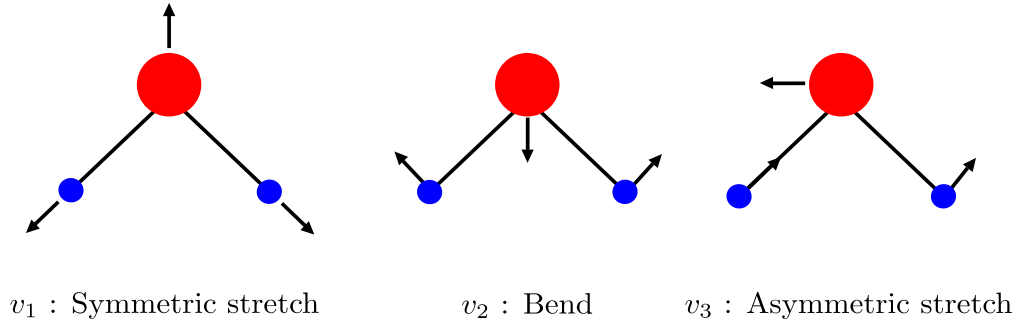


Figure 2.7: Representation of the three vibrational modes of the water molecule following Herzberg notation.

Where $|J, k, m\rangle$ are the wavefunctions of the symmetric basis set and c_k the coefficient of the linear combination. Owing to the fact that a function that is the sum of different functions will have a symmetry that is the combination of the ones of these functions, it can be said that the symmetry of the wavefunction ψ_{rot} is a combination of the ones of $|J, k, m\rangle$. It is therefore required to determine the symmetry of these functions $|J, k, m\rangle$.

The symmetry operations that will be used here are the symmetry operations that belong to the spatial group K that contains all the rotations operations. All the rotations that will be involved herebelow will be expressed in terms of two equivalent rotations.

R_z^β : Rotation of an angle β about the z axis

R_α^π : Rotation of 180° about an axis in the xy plane; this axis forms an angle α with the x axis.

The effect of these rotations on the wavefunctions $|J, k, m\rangle$ have to be considered in order to determine the character of these wavefunctions under these symmetry operations. These wavefunctions are expressed [23] in terms of the three Euler angles θ, ϕ, χ by

$$|J, k, m\rangle = X_{Jkm} \exp(im\phi) \exp(ik\chi) \left\{ \sum_{\sigma} (-1)^{\sigma} \frac{(\cos \theta/2)^{2J=k-m-2\sigma} (-\sin \theta/2)^{m-k+2\sigma}}{\sigma! (J-m-\sigma)! (m-k-\sigma)! (J+k-\sigma)!} \right\} \quad (2.40)$$

with

$$X_{Jkm} = [(J+m)! (J-m)! (J+k)! (J-k)! (2J+1) / (8\pi^2)]^{1/2} \quad (2.41)$$

The two equivalent rotations defined above will only affects the Euler angles. It is therefore possible to consider their influence on the symmetric top wavefunctions of the basis set only in terms of these Euler angles. This is done in equation (2.42).

$$\begin{cases} R_z^\beta(\theta, \phi, \chi) = (\theta, \phi, \chi + \beta) \\ R_\alpha^\pi(\theta, \phi, \chi) = (\pi - \theta, \phi + \pi, 2\pi - 2\alpha - \chi) \end{cases} \quad (2.42)$$

The effect of these rotations on the symmetric top wavefunctions are given in equation (2.43).

$$\begin{cases} R_z^\beta |J, k, m\rangle = e^{ik\beta} |J, k, m\rangle \\ R_\alpha^\pi |J, k, m\rangle = (-1)^J e^{-2ik\alpha} |J, -k, m\rangle \end{cases} \quad (2.43)$$

Two limits will be considered to study the symmetry of the H_2O molecule. The first one is the prolate limit that considers $I_a < I_b = I_c$, the second one is the oblate limit that considers

$I_a = I_b < I_c$. For the first limit one will consider the first choice of relation between the xyz and the abc axis system (xyz=bca) whereas for the second limit one will choose the second one (xyz=abc).

Prolate limit

Each of the symmetry operations of the point group of the water molecule can be written as an equivalent rotation thanks to the isomorphism between the point group $\mathcal{G}$ and the spatial group $\mathcal{K}$, this is summarised in Table 2.8.

Symmetry operation	R_α^π form
$\hat{E}$	R^0
$\hat{C}_2$	R_0^π
$\hat{\sigma}_v$	$R_{\pi/2}^\pi$
$\hat{\sigma}_{v'}$	R_z^π

Table 2.8: Isomorphism between the symmetry operation of the C_{2v} point group and rotations in the prolate limit.

Let us now study the effect of each of these operations on $|J, k, m\rangle$ in order to determine the characters of this representation under these operations and thus the symmetry of the wavefunction. In the prolate limit, the convention between the axis systems is such that $z=a$ and therefore $k = k_a$. The obtained results are given in (2.44).

$$\begin{cases} R^0 : & |J, k_a, m\rangle = |J, k_a, m\rangle \\ R_x^\pi : & |J, k_a, m\rangle = (-1)^J |J, -k_a, m\rangle \\ R_y^\pi : & |J, k_a, m\rangle = (-1)^{J+k_a} |J, -k_a, m\rangle \\ R_z^\pi : & |J, k_a, m\rangle = (-1)^{k_a} |J, k_a, m\rangle \end{cases} \quad (2.44)$$

The characters of this representation can be discussed as a function of k_a , this is done in Table 2.9 where the equivalent rotations are expressed in terms of the R_α^π convention. These characters have been obtained by applying the different equivalent rotations to $|J, k_a, m\rangle$ and $|J, -k_a, m\rangle$ for $k_a \neq 0$.

	R^0	R_x^π	R_y^π	R_z^π
$k_a = 0$	1	$(-1)^J$	$(-1)^J$	1
$k_a \neq 0$	2	0	0	$2(-1)^{k_a}$

Table 2.9: Characters of the rotational wavefunctions for different values of k_a and J in the prolate limit. The rotations are expressed in terms of the R_α^π convention

Oblate limit

Each of the symmetry operations of the point group of the water molecule can also be written as an equivalent rotation in the oblate limit, this is resumed in Table 2.10.

Symmetry operation form	R_α^π form
$\hat{E}$	R^0
$\hat{C}_2$	$R_{\pi/2}^\pi$
$\hat{\sigma}_v$	R_z^π
$\hat{\sigma}_{v'}$	R_0^π

Table 2.10: Isomorphism between the symmetry operations of the C_{2v} point group and rotations in the oblate limit.

Let us now study the effect of each of these operations on $|J, k, m\rangle$ in order to determine the characters of this representation under these operations and thus the symmetry of the wavefunction. In the oblate limit, the convention between the axis systems is such that $z=c$ and therefore $k = k_c$. The obtained results are given in (2.45).

$$\begin{cases} R^0 : & |J, k_c, m\rangle = |J, k_c, m\rangle \\ R_y^\pi : & |J, k_c, m\rangle = (-1)^{k_c} |J, -k_c, m\rangle \\ R_z^\pi : & |J, k_c, m\rangle = (-1)^{J+k_c} |J, -k_c, m\rangle \\ R_x^\pi : & |J, k_c, m\rangle = (-1)^J |J, k_c, m\rangle \end{cases} \quad (2.45)$$

The characters of this representation can be discussed as a function of k_c , this is done in Table 2.11. These characters have been obtained by applying the different equivalent rotations to $|J, k_c, m\rangle$ and $|J, -k_c, m\rangle$ for $k_c \neq 0$.

	R^0	R_y^π	R_z^π	R_x^π
$k_c = 0$	1	$(-1)^J$	1	$(-1)^J$
$k_c \neq 0$	2	0	$2(-1)^{k_c}$	0

Table 2.11: Characters of the rotational wavefunctions for different k_c and J values in the oblate limit. The rotations are expressed in terms of R_α^π convention

Asymmetric top molecule

It is now possible to discuss the symmetry of the rotational wavefunctions in both the prolate and the oblate limit as a function of the values of k_a and k_c . More precisely, it is the parity of k_a and k_c that determines this symmetry. Indeed, depending on these parities the character of the representation of the wavefunction under the transformations $\hat{\sigma}_v$ and $\hat{\sigma}_{v'}$ will be 2 or -2 . Tables 2.12 and 2.13 summarise the symmetries in the prolate and oblate limits, respectively, of the rotational wavefunction of the water molecule as a function of J , k_a and k_c .

Condition	Symmetry
$k_a = 0, J$ even	A_1
$k_a = 0, J$ odd	B_1
$k_a \neq 0$ even	$A_1 \oplus B_1$
$k_a \neq 0$ odd	$A_2 \oplus B_2$

Table 2.12: Symmetry of the rotational wavefunctions of H_2O in the prolate limit.

Condition	Symmetry
$k_c = 0, J$ even	A_1
$k_c = 0, J$ odd	B_2
$k_c \neq 0$ even	$A_1 \oplus B_2$
$k_c \neq 0$ odd	$A_2 \oplus B_1$

Table 2.13: Symmetry of the rotational wavefunctions of H_2O in the oblate limit.

The water molecule being an asymmetric top molecule, it can neither be considered totally prolate or oblate. The determination of the symmetry of a rotational state of the asymmetric top wavefunction $|J, k_a, k_c\rangle$ is based on the correlation between the prolate and oblate wavefunctions

$|J, k_a, m\rangle$ and $|J, k_c, m\rangle$. This correlation is shown in Figure 2.8. The symmetry representation of an asymmetric top state is the one that is common to both of its prolate and oblate limit representations.

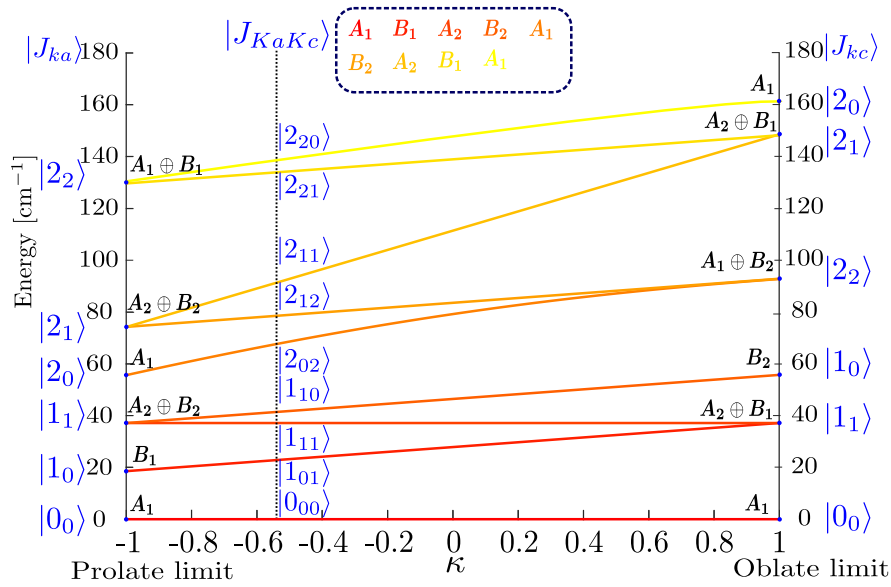


Figure 2.8: Correlation of the asymmetric top states with their prolate and oblate limits. The dashed line corresponds to the asymmetry parameters of the water molecule. The representations of each oblate and prolate state are indicated next to the considered state. The representations of the asymmetric top molecules are given in the legend box.

Table 2.14 gives the rotational symmetry of the H_2O molecule considered as an asymmetric top molecule. One can see that the only parameters that influence this symmetry are the parity of K_a and K_c .

$K_a K_c$	Γ_{rot}
even, even	A_1
odd, odd	A_2
even, odd	B_1
odd, even	B_2

Table 2.14: Symmetry of the rotational wavefunction of H_2O as a function of K_a and K_c .

2.4.3.4 Symmetry of the nuclear spin wavefunctions

The last wavefunctions whose symmetry have to be investigated are the nuclear spin wavefunctions. They characterise the spin of the nuclei contained in the molecule. In the case of H_2O , there are two atoms of hydrogen and one of oxygen. In terms of $|I, m_I\rangle$, I being the nuclear spin angular momentum and m_I its projection, the possible wavefunctions for H are $\alpha = |1/2, 1/2\rangle$ and $\beta = |1/2, -1/2\rangle$ whereas the one for O is $\delta = |0, 0\rangle$. The combinations of these wavefunctions allow to determine four nuclear spin wavefunctions for the water molecule.

$$\begin{aligned}
\psi_{\text{nspin}, 1} &= \alpha\alpha\delta \\
\psi_{\text{nspin}, 2} &= \beta\beta\delta \\
\psi_{\text{nspin}, 3} &= \alpha\beta\delta \\
\psi_{\text{nspin}, 4} &= \beta\alpha\delta
\end{aligned}$$

The last two ones are not orthonormal to the others one. In order to obtain an orthonormal basis set, it is necessary to orthogonalise them. The set of orthogonalised nuclear spin wavefunctions is therefore given by

$$\begin{aligned}
\psi_{\text{nspin}, 1} &= \alpha\alpha\delta \\
\psi_{\text{nspin}, 2} &= \beta\beta\delta \\
\psi_{\text{nspin}, 3} &= \frac{1}{\sqrt{2}} (\alpha\beta + \beta\alpha) \delta \\
\psi_{\text{nspin}, 4} &= \frac{1}{\sqrt{2}} (\alpha\beta - \beta\alpha) \delta
\end{aligned}$$

In order to find their symmetry, it is necessary to determine how they are modified by the symmetry operations of the molecular symmetry group $C_{2v}(M)$. The first three wavefunctions belong to the A_1 representation whereas the last one belongs to the B_2 because its sign changes under the operations (12) and E^* . One can thus write

$$\Gamma_{\text{nspin}} = 3A_1 \oplus B_2 \quad (2.46)$$

The multiplicative terms 3 and 1 that appear in equation (2.46) are the so called statistical weights. They mean that there are three times more nuclear spin wavefunctions of A_1 irreducible representation than B_2 . Once combined with the other components of the total wavefunction this will influence population ratio between states.

2.4.3.5 Symmetry of the molecular wavefunction

The symmetry of the molecular wavefunction of H_2O is determined by the direct product of the ones of the electronic, rotational, vibrational and nuclear spin wavefunctions. This can be expressed as in equation (2.47).

$$\Gamma_{\text{tot}} = \Gamma_{\text{elec}} \otimes \Gamma_{\text{rot}} \otimes \Gamma_{\text{vib}} \otimes \Gamma_{\text{nspin}} \quad (2.47)$$

The symmetry of the different representations that appear in equation (2.47) can vary as a function of certain quantum numbers (J , K_a and K_c for Γ_{rot} and ν_3 for Γ_{vib}). This is why the representation to which the total wavefunction belongs is not unique. Each rovibronic state will be characterised by a different symmetry for this wavefunction. The symmetry of these rovibronic states will be essential in the computation of the spectrum of H_2O .

Before going further in the computation of the spectrum, it is interesting to briefly consider the Pauli exclusion principle. This principle states that two fermions cannot be in the same quantum state. If one consider the water molecule, the hydrogen atoms are fermions because their spin is half integer. This means that if the two hydrogen atoms are interchanged the wavefunction has to change too. This is mathematically expressed by

$$(12) \psi_{\text{H}_2\text{O}} = -\psi_{\text{H}_2\text{O}} \quad (2.48)$$

Considering Table 2.6, this means that the total wavefunction of the water molecule must either be of symmetry B_1 or B_2 . This implies that, depending on the symmetry of the rotational and vibrational wavefunctions, the molecular wavefunction of the water molecule will belong to one or other configuration.

On the contrary, when considering the molecule D_2O , the deuterium atoms are bosons and thus the symmetry operation (12) will leave the wavefunction unchanged.

$$(12) \psi_{D_2O} = \psi_{D_2O} \quad (2.49)$$

This means that the total wavefunction of this molecule will either belong to representation A_1 or to A_2 .

The symmetry of the molecular wavefunction can be summarised as a function of the symmetries of the different wavefunctions ψ_{rot} , ψ_{vib} , ψ_{elec} and ψ_{nspin} . The symmetry of the molecular wavefunction is also ruled by the Pauli exclusion principle that implies that this wavefunction either belongs to B_1 or to B_2 . Table 2.15 gathers the different possible combinations of symmetries for the different wavefunctions of the water molecule as a function of the parity of K_a and K_c . These combinations are considered in the fundamental vibrational and electronic state which implies that the symmetry of both of the corresponding wavefunctions is A_1 .

$K_a K_c$	Γ_{rot}	Γ_{vib}	Γ_{elec}	Γ_{nspin}	Γ_{tot}	Statistical weights
ee	A_1	A_1	A_1	B_2	B_2	1
eo	B_1	A_1	A_1	A_1	B_1	3
oo	A_2	A_1	A_1	B_2	B_1	1
oe	B_2	A_1	A_1	A_1	B_2	3

Table 2.15: Summary of the symmetry representations as a function of the parity of K_a and K_c for the water molecule in its fundamental vibrational and electronic state.

2.4.4 Computation of the spectrum

The spectrum of a molecule provides information about the allowed transitions between any pair of its rovibronic states. Indeed, the positions of the spectrum lines give the difference of energy of the allowed transitions whereas the intensities of these lines give information on the strength of these transitions related to line strength, population and statistical weights. We would like to simulate the spectrum of H_2O . In order to do this, it is required to determine the allowed transitions as well as their intensities. The determination of the allowed transitions is based on the symmetry of the representation generated by the wavefunction and the vanishing integral rule. This rule says that to be allowed a transition must fulfils the following relation

$$\Gamma_{\psi'} \otimes \Gamma^* \otimes \Gamma_{\psi''} \supset A_1 \quad \leftrightarrow \quad \langle \psi' | \mu_A | \psi'' \rangle \neq 0 \quad (2.50)$$

Where the terms $\Gamma_{\psi'}$, Γ^* and $\Gamma_{\psi''}$ are the representations generated by the final state, the dipole moment and the initial state respectively. If this relation is fulfilled, the transition is allowed, otherwise the transition is forbidden.

2.4.4.1 Determination of the selection rules

A transition is said to be allowed if the representation generated by the matrix element (see equation (2.50)) contains the totally symmetric representation A_1 . If one assumes that the wavefunctions of the initial and final states can be expressed as a product of rotational, vibrational, electronic and nuclear spin wavefunctions, equation (2.50) can be rewritten as

$$\langle \psi' | \hat{\mu}_A | \psi'' \rangle = \langle \psi'_{\text{elec}} \psi'_{\text{rot}} \psi'_{\text{vib}} \psi'_{\text{espin}} \psi'_{\text{nspin}} | \hat{\mu}_A | \psi''_{\text{elec}} \psi''_{\text{rot}} \psi''_{\text{vib}} \psi''_{\text{espin}} \psi''_{\text{nspin}} \rangle \quad (2.51)$$

The vanishing integral rule can be expressed in terms of representation theory.

$$\Gamma'_{\text{elec}} \otimes \Gamma'_{\text{rot}} \otimes \Gamma'_{\text{vib}} \otimes \Gamma'_{\text{nspin}} \otimes \Gamma_{\mu_A} \otimes \Gamma''_{\text{elec}} \otimes \Gamma''_{\text{rot}} \otimes \Gamma''_{\text{vib}} \otimes \Gamma''_{\text{nspin}} \supset \mathbf{A}_1 \quad (2.52)$$

If one considers that the initial state belong to the vibrational ground state $v_1 = v_2 = v_3 = 0$ and if one considers that these transitions cannot change the symmetry of the total nuclear spin of the molecule. This means that Γ''_{nspin} and Γ'_{nspin} must have the same irreducible representation implying that $\Delta I = \Delta m_I = 0$. By looking at the $C_{2v}(M)$ character table, one can see that the symmetry of $\hat{\mu}_A$ is $\mathbf{A}_2$.

Let us firstly consider the case for which v_3 of the final state is even, which means that $\Gamma'_{\text{vib}} \subset \mathbf{A}_1$. Equation (2.52) can thus be rewritten

$$\begin{aligned} \mathbf{A}_1 \otimes \Gamma'_{\text{rot}} \otimes \mathbf{A}_1 \otimes \Gamma'_{\text{nspin}} \otimes \mathbf{A}_2 \otimes \mathbf{A}_1 \otimes \Gamma''_{\text{rot}} \otimes \mathbf{A}_1 \otimes \Gamma''_{\text{nspin}} &= \mathbf{A}_2 \otimes \Gamma'_{\text{rot}} \otimes \Gamma'_{\text{nspin}} \otimes \Gamma''_{\text{rot}} \otimes \Gamma''_{\text{nspin}} \\ &= \mathbf{A}_2 \otimes \Gamma'_{\text{rot}} \otimes \Gamma''_{\text{rot}} \otimes \underbrace{\Gamma''_{\text{nspin}} \otimes \Gamma'_{\text{nspin}}}_{\mathbf{A}_1} \\ &= \mathbf{A}_2 \otimes \Gamma'_{\text{rot}} \otimes \Gamma''_{\text{rot}} \end{aligned}$$

In order to fulfil the vanishing integral rule, the direct product $\Gamma''_{\text{rot}} \otimes \Gamma'_{\text{rot}}$ has to contain the representation $\mathbf{A}_2$. There are two different ways to obtain this representation by a direct product of two representations. The first one is obtained by $\mathbf{A}_1 \otimes \mathbf{A}_2 = \mathbf{A}_2$ and the second one is obtained by $\mathbf{B}_1 \otimes \mathbf{B}_2 = \mathbf{A}_2$. By looking back at Table 2.14, it can be said that in both cases, both $|\Delta K_a|$ and $|\Delta K_c|$ are odd.

The second case that has to be considered is the one for which v_3 of the final state is odd, which means that $\Gamma'_{\text{vib}} \subset \mathbf{B}_2$. Equation (2.52) can thus be rewritten

$$\begin{aligned} \mathbf{A}_1 \otimes \Gamma'_{\text{rot}} \otimes \mathbf{B}_2 \otimes \Gamma'_{\text{nspin}} \otimes \mathbf{A}_2 \otimes \mathbf{A}_1 \otimes \Gamma''_{\text{rot}} \otimes \mathbf{A}_1 \otimes \Gamma''_{\text{nspin}} &= \mathbf{B}_1 \otimes \Gamma'_{\text{rot}} \otimes \Gamma'_{\text{nspin}} \otimes \Gamma''_{\text{rot}} \otimes \Gamma''_{\text{nspin}} \\ &= \mathbf{B}_1 \otimes \Gamma'_{\text{rot}} \otimes \Gamma''_{\text{rot}} \otimes \underbrace{\Gamma''_{\text{nspin}} \otimes \Gamma'_{\text{nspin}}}_{\mathbf{A}_1} \\ &= \mathbf{B}_1 \otimes \Gamma'_{\text{rot}} \otimes \Gamma''_{\text{rot}} \end{aligned}$$

The term $\mathbf{B}_1$ that appears at the first line is obtained by $\mathbf{B}_2 \otimes \mathbf{A}_2 = \mathbf{B}_1$. In order to fulfil the vanishing integral rule, the direct product $\Gamma''_{\text{rot}} \otimes \Gamma'_{\text{rot}}$ has to contain the representation $\mathbf{B}_1$. There are two different ways to obtain this representation by a direct product of two representations. The first one is $\mathbf{A}_1 \otimes \mathbf{B}_1 = \mathbf{B}_1$ and the second one is $\mathbf{A}_2 \otimes \mathbf{B}_2 = \mathbf{B}_1$. By looking back at Table 2.14, it can be said that in both cases $|\Delta K_a|$ is even and $|\Delta K_c|$ is odd.

Table 2.16 summaries the selection rules that allow a given transition, they are split in both cases developed here above.

$v_{3,\text{final}}$ even	$v_{3,\text{final}}$ odd
$ \Delta K_a $ odd and $ \Delta K_c $ odd	$ \Delta K_a $ even and $ \Delta K_c $ odd
$\Delta J = -1, 0, 1$	

Table 2.16: Selection rules for the H_2O molecule.

This set of selection rules determines the allowed transitions between the set of rovibronic states. All the transitions that fulfill these conditions will be considered as allowed transitions and will therefore have a non zero intensity.

2.4.4.2 Computation of the intensity of the transitions

The rovibronic spectrum of a given molecule is characterised by transitions that occur at given energies and of given intensities. The energies of these transitions depend on the difference of energy between the initial and the final states. The intensity of the transitions depends on other parameters than the ones derived in section 2.4.4.1. In order to study this dependence, it is necessary to look at the wavefunctions basis set on which the ro-vibrational wavefunctions are built. The wavefunctions and the development achieved hereafter are based on the method developed by Sutcliffe and Tennyson[26]. The internal coordinates of interest for the water molecule are the bond lengths r_1 and r_2 as well as the angle θ between these bonds. The rotational part of the wavefunctions are expressed by the Condon and Shortley functions $\Theta_{jk}(\theta)$ coupled with Wigner rotation matrices $D_{Mk}^J(\alpha, \beta, \gamma)$ where α , β and γ are the so called Euler angles. It is also necessary to introduce p the parity quantum number that can take the value 0 or 1. The basis set corresponding to the rotational part of the wavefunctions is given by equation (2.54)[27].

$$|J_M, k, j, p\rangle = (-1)^k \left(\frac{2J+1}{8\pi^2} \right)^{1/2} (1/2)^{1/2} \left\{ \Theta_{jk}(\theta) D_{Mk}^{*J}(\alpha, \beta, \gamma) \right\} \\ + (-1)^p \Theta_{j-k}(\theta) D_{Mk}^{*J}(\alpha, \beta, \gamma), \quad k > 0, p = 0, 1 \quad (2.53)$$

$$|J_M, 0, j, p\rangle = \left(\frac{2J+1}{8\pi^2} \right)^{1/2} \Theta_{j0}(\theta) D_{M0}^{*J}(\alpha, \beta, \gamma), \quad k = 0, p = 0 \quad (2.54)$$

The vibrational part of the wavefunctions basis set is represented by the product of Morse oscillator like functions $\phi_m(r_1)\phi_n(r_2)$. In order to ease further expressions, this product can be shortened as expressed in equation (2.55).

$$|n, m\rangle = \phi_m(r_1)\phi_n(r_2) \quad (2.55)$$

The basis set being defined, it is possible to express an eigenfunction with angular momentum J and parity p by equation (2.56).

$$|J_M, p, l\rangle = \sum_{k=p}^J \sum_{jmn} d_{kjm n}^{J M p l} |J_M, k, j, p\rangle |m, n\rangle \quad (2.56)$$

Where $d_{kjm n}^{J M p l}$ are the coefficient involved in the linear combination of the considered wavefunction.

The line strength of a given transition between an initial state i and a final state f will depend on the wavefunctions of these states as well as of the τ component of the space-fixed dipole moment. One has

$$S(f-i) = \sum_{M' M'' \tau} \left(T_{if}^{M' M'' \tau} \right)^2 \quad (2.57)$$

$$\text{where } T_{if}^{M' M'' \tau} = \langle J'_{M'}, p', l' | \mu_{\tau}^s | J''_{M''}, p'', l'' \rangle \quad (2.58)$$

Additional calculations [28] allow to express this line strength by introducing some other quantities. By defining $\lambda = |v|$, it is possible to write the line strength as follows

$$\begin{aligned}
S(f-i) &= \frac{1}{4} [(2J' + 1)(2J'' + 1)] \\
&\times \left[\sum_{v=-1}^{+1} \sum_{\lambda=|v|} \sum_{k=p''}^{J''} \sum_{j''}^{J''} a(v, v+k, \lambda) [(2j' + 1)(2j'' + 1)]^{1/2} \right. \\
&\times \begin{pmatrix} J' & 1 & J'' \\ -k-v & v & k \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ -k-v & v & k \end{pmatrix} \\
&\times \sum_{m''n''} \sum_{m'n'} B_{\lambda,v}^{m'm''n'n''} \times d_{k'j'm'n'}^{j'p'l'} d_{k''j''m''n''}^{j''p''l''} \left[(-1)^{J''+J'+1} + (-1)^{p''+p'} \right] \left. \right]^2 \quad (2.59)
\end{aligned}$$

We define the term $a(v, v+k, \lambda)$ by equation (2.60).

$$\begin{cases} a(0, n, \lambda) &= 1 \\ a(\pm 1, 0, \lambda) &= -[\lambda(\lambda+1)]^{1/2} \\ a(\pm 1, n, \lambda) &= -[\lambda(\lambda+1)/2]^{1/2} \\ a(v, n, \lambda) &= 0, \quad n < 0, \quad n > J', \quad v = 0, \pm 1 \end{cases} \quad (2.60)$$

The line strength also depends on the angular momentum of the initial and final states concerned by the transition, respectively J'' and J' . The matrices involved in equation (2.59) are the so called 3-j Wigner symbols. They are defined by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}} \langle j_1 m_1 j_2 m_2 | j_3 (-m_3) \rangle \quad (2.61)$$

The terms $d_{k'j'm'n'}^{j'p'l'}$ and $d_{k''j''m''n''}^{j''p''l''}$ are the coefficients that appear in the linear combination expressing a given eigenfunction in terms of the ones of the basis set. The term $B_{\lambda,v}^{m'm''n'n''}$ can be understood as the mean value of the Legendre expansion of the $v = 0$ and $v = 1$ dipole moment surface. In other words, it can be written as equation (2.62).

$$B_{\lambda,v}^{m'm''n'n''} = \langle m'n' | C_{\lambda,v}(r_1, r_2) | m''n'' \rangle \quad (2.62)$$

The integrated absorption coefficient can be derived from the line strength and other parameters such as the degenerescence due to the spin statistical weights g_i , Avogadro's number N_A or the transition frequency ω_{if} . Equation (2.63) gives the expression of the molar absorption coefficient in terms of these parameters.

$$\alpha(\omega_{if}) = \frac{8\pi N_A \omega_{if} (2J_i + 1) g_i \exp(-E''/kT) [1 - \exp(hc\omega_{if}/kT)]}{3hQ} \Phi(\omega_{if}) S(f-i) \quad (2.63)$$

The term Q that appears in equation (2.63) is the partition function given by

$$Q = \sum_i g_i (2J_i + 1) \exp(-E_i/kT)$$

This sum runs on all the fundamental rotational states. These states have been chosen such that $v_1 = v_2 = v_3 = 0$ and $J \leq 8$. This sum has been truncated at this value of J because the states whose $J \geq 8$ are not considered as fundamentals since their population at ambient temperature are too low to be considered.

2.4.5 Simulation of the absorption spectrum of the water molecule

The absorption spectrum of the water molecule has been simulated using selection rules and intensities developed in sections 2.4.4.1 and 2.4.4.2. The position of the simulated transitions simulated is supposed to be correct because the selection rules have been verified with the ones detailed in [23]. The intensity of the computed transitions is different than the ones obtained by Hitran. Indeed, the last line of equation (2.59) has been considered as constant because we did not find any parameter in the literature. This term can however be intuitively understood. For each of the final vibrational bands (the initial vibrational band is only composed of the fundamental one) there is a different factor. This factor is determined by the term that has been held constant in equation (2.59). Figure 2.9 compares the transitions obtained by simulation for the vibrational band $v_1v_2v_3 = 311$ in the wavenumber range between 15380 and 15410 cm^{-1} with the same frequency range as the spectrum simulated by Hitran.

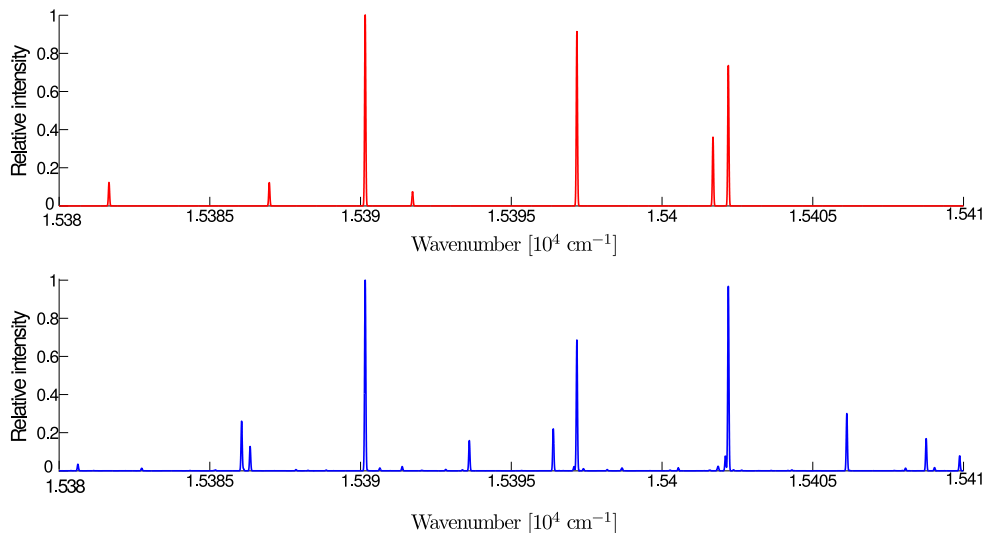


Figure 2.9: Transitions obtained by simulations (in red on top of the figure) and by Hitran (in blue in the bottom of the figure) for the water molecule at $T=296\text{K}$ and $p \approx 1\text{atm}$. The computed lines are the ones that belong to the final vibrational states $v_1v_2v_3 = 311$.

The simulation of the absorption spectrum has been performed on the basis of fundamental states whose energies have been obtained thanks to the diagonalisation of the rigid rotor Hamiltonian and on the basis of excited states that are due the one provided in the supplementary material of Ref. [25]. This simulation is therefore based on partially homemade values of energy levels.

Figure 2.9 shows that the relative intensities of the lines in the Hitran spectrum and in the simulation do not correspond. This phenomenon is due to the term of equation (2.59) that has not been taken into account in the computation of the intensities. This term involves the integration of the dipolar moment on potential surfaces. It therefore requires to compute these surfaces and then to integrate the dipolar moment on them. The implementation of this term has not been implemented because of a lack of time.

The obtained absorption spectrum however looks like the one generated by Hitran. Some differences can nevertheless be noticed between these two spectra. They are due to the absence of this term in the computation of the intensity. The analysis of the spectra of Figure 2.9 allows to say that the influence of this term is large enough to make appear and disappear some lines in the simulated spectrum.

The position of the transitions computed by the simulation can however be compared to the ones of the spectrum obtained on the basis on the Hitran database. These positions can also be compared to the ones presented in Ref. [29]. These two comparisons allow to say that the position of the lines in the simulated spectrum are correct. This means that the selection rules derived are correct too.

Experimental setup and data analysis

3.1 Description of the experimental set-up

This section details the cavity ring-down spectrometer that was built up as a part of this master thesis. A general scheme of the experimental set-up is depicted in Figure 3.1 and a photography of the real experimental set-up is shown in Figure 3.2. Both of these representations of the set-up involve circled numbers that refer to the different parts used. The light source used to perform the spectroscopy is a dye laser pumped by the second harmonic of a Nd:YAG laser ①. The light beam emitted by this laser goes through a dichroic mirror ② and through the first lens used for the mode matching ③. A mirror ④ reflects then the beam through a $\lambda/4$ waveplate ⑤ to a second mirror ⑥. This second mirror reflects the beam through the second lens of the mode matching ⑦ and the beam is then injected inside the cell ⑨ through the back of one of the two mirrors of the cavity ⑧. The fraction of the light that exits the cavity is detected by a photomultiplier ⑩ that transforms the light intensity into electric signal for the data processing ⑪.

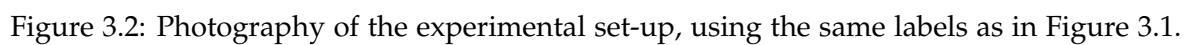
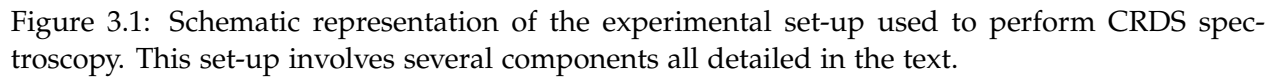
From a geometrical point of view, the most important distances are the one between the output of the laser and the first lens required for the mode matching d_1 , the one between the two lenses required for the mode matching d_2 and the one between the second lens and the back side of the entry mirror of the cavity d_3 . Indeed, these three distances, represented in Figure 3.1 are the ones that have been computed in order to perform a correct mode matching (see section 1.5). However, due to experimental constraints, it was not possible to set the elements apart at the distances computed by the mode matching resolution. They were respectively set to $d_1 = 55$ cm, $d_2 = 25$ cm and $d_3 = 9$ cm¹ instead of $d_1 = 49.9$ cm, $d_2 = 26$ cm and $d_3 = 12$ cm in the computations. This mismatch is nevertheless less critical than the case where there is no mode matching at all.

Some of the components involved in Figures 3.1 and 3.2 need to be briefly explained. The laser used for the experiments is a dye laser pulsed at a frequency of 30 Hz with pulses of few nanoseconds long. This means that the intensity of the beam at the output of the laser and the one at the output of the cavity will respectively look like the ones in Figures 3.3 and 3.4. The wavelength of the laser can be scanned through a certain wavelength range. Two main wavelength ranges were studied: a first one from 628.15 to 631 nm and a second one from 648.5 to 650 nm.

The dichroic mirror ② acts as a filter in order to only keep the wavelengths at which the gas contained in the cell has to be investigated. Indeed, the dye laser being pumped by a green laser², a small amount of green light will be transmitted at the output of the laser. The dichroic mirror

¹These measures were performed with a measuring tape and are so precise to ± 1 mm

²This green laser is the second harmonic of a Nd:YAG laser.



The interest of the mode matching optics has already been explained in section 1.5.

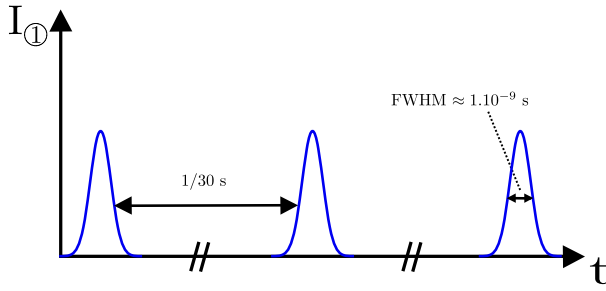


Figure 3.3: Signal at the output of the dye laser.

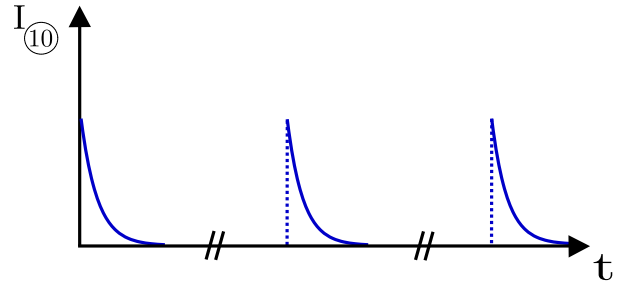


Figure 3.4: Signal at the exit of the optical cavity.

The $\lambda/4$ waveplate ⑤ induces a phase lag to the wave of a quarter of wavelength which means that the light that goes back towards the laser has not the same polarisation as the one of the laser.

The cell surrounded by the cavity ⑨ will vary as a function of the measurements that have to be achieved. If the measurements have to be achieved at ambient temperature and pressure, a simple PVC pipe can be used³, its aim is to avoid contamination of the cavity by external light sources. The gas contained in this cell is the same as the one that fills the laboratory. It is thus air with the same composition, temperature and pressure as ambient air. The cavity used in the experimental set-up will vary if the measurements have to be performed at low pressure or at low temperature. The cavity used to perform measurements at low temperature is the one discussed in section 3.3.3 and is represented in Figure 3.5.

The last component present on the optical table is the photomultiplier ⑩ whose role is to detect the light at the output of the cavity. The intensity of this light is very weak, therefore the photomultiplier has to be combined with a fast amplifier. This photomultiplier will transform the light intensity in an electric current and afterwards in a tension which can be recorded by a fast oscilloscope [30]. The data from the oscilloscope are transferred to a computer and processed with a LABVIEW routine detailed in appendix B. This detector is of prime importance because it determines the lower intensity that can be detected by the set-up.

3.1.1 Characterisation of the detectors

The detectors used in this experimental set-up have been characterised. This section details the characterisation procedure as well as its results. Two detectors were used in the set-up but only one was utilised to obtain the results presented afterwards. These two detectors have undergone the same tests. They are shown in Figure 3.6, the one to the left of this photography is the one that has been used to perform the absorption spectrum measurements whereas the one on the right of this photography is the one designed by Marc DAMAN that will be used in future measurements.

3.1.1.1 Procedure

The aim of this procedure is to determine whether the detectors located at the output of the cavity corrupt the signal or not. Indeed, the detectors could be inefficient in the measurement of signals depending on the signal frequency. The detectors could also modify the signal by filtering and modifying it. The two steps of the procedure described here after are respectively designed to verify these two assumptions.

³This is the one present in Figure 3.2

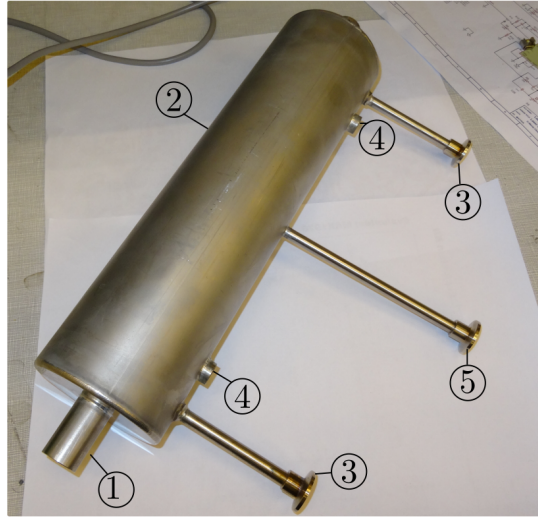


Figure 3.5: Cryogenic cell designed and built for this master thesis by Daniel DEDOUAIRE. The inner ① and outer ② cylinders are visible, however the intermediate cylinder is hidden. The system used to create the flux of liquid nitrogen ③ as well as the one used to pump down the outer cylinder ⑤ also are represented in this figure. The system used to create the flux of gas inside the cavity ④ is also shown.

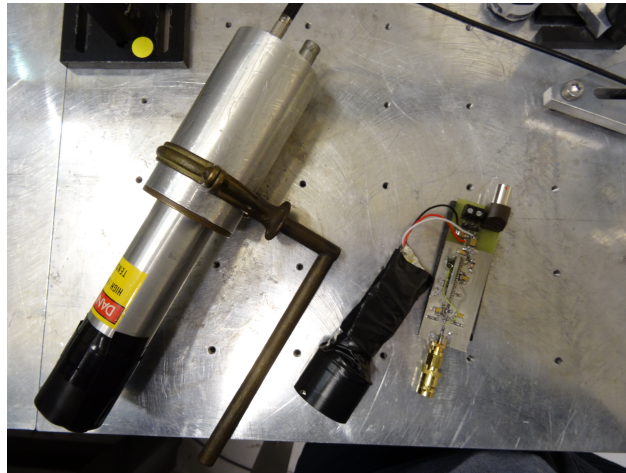


Figure 3.6: Photography of the two photomultipliers that have been tested. The circuit connected to the smaller photomultiplier is an amplifier.

3.1.1.2 Characterisation of the detector bandwidth

In order to determine the bandwidth of the detectors, a particular experimental set-up has been established. A diode laser has been used as light source. This diode is controlled by a square signal of tunable frequency. The investigated frequency range is from 5 to 300 kHz. This frequency range has been chosen because the measured signal in the CRDS experiment is 2-3 μs

long whereas the one that should theoretically be obtained has a duration of about $200 \mu s$.

The light emitted by the diode laser is measured by the detector which is connected to an oscilloscope that displays the signal measured by the photomultiplier connected to an oscilloscope in order to study the measured signal. This experimental set-up is shown in Figure 3.7.

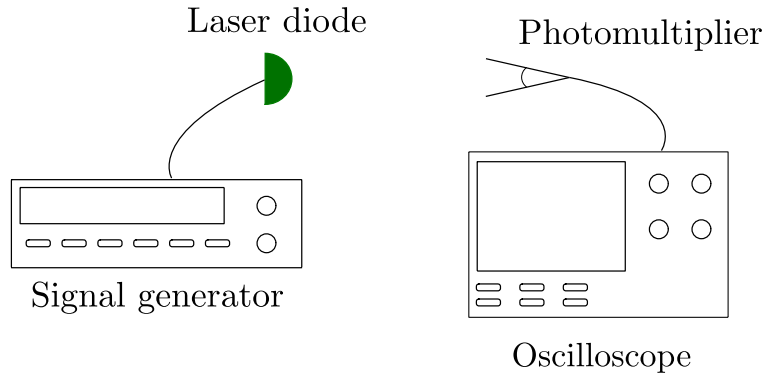


Figure 3.7: Schematic representation of the experimental set-up used to determine the bandwidth of the detectors.

The diode laser has been used with a square signal of 4V of amplitude and an offset of 3V. It was considered that the photomultiplier detects the considered frequency if the frequency of the signal represented on the oscilloscope is the same as the one generated by the signal generator. All the probed frequencies were detected even though different tensions have to be applied to the photomultiplier. Table 3.1 gives the tensions that had to be applied in order to detect the signal for the different investigated frequencies.

Frequency [kHz]	5	10	25	50	100	150	200	250	300
Tension applied on the photomultiplier	600	600	700	700	800	800	800	800	800

Table 3.1: Tensions applied on the photomultiplier for different frequencies in order to detect the signal.

3.1.1.3 Determination of the filtering of the signal

The second step consists in the determination of an eventual modification of the experimental signal. The same experimental set-up as in Figure 3.7 was used. The signal applied to the diode laser is an exponential signal that will allow to perform an exponential fit on the measured signal thanks to the LABVIEW routine. The characteristic time of the exponential signal generated by the signal generator is known and compared to the one obtained by the exponential fit performed by the computer. If these times are close enough to one another, the signal is not modified by the detector.

A signal generated by the signal generator and detected by the photomultiplier is represented in Figure 3.8. The exponential behaviour of this signal is not obvious due to a filtering effect of the diode laser. However by performing to an exponential fitting in the blue window, it is possible to obtain a characteristic time close enough to the one generated by the signal generator to be considered equal.

The two detectors investigated by these two characterisation steps give encouraging results. Indeed, in both cases, the bandwidth of the detectors is broad enough to contain the investigated bandwidth. Moreover, for both detectors, the exponential signals were not affect by the detection

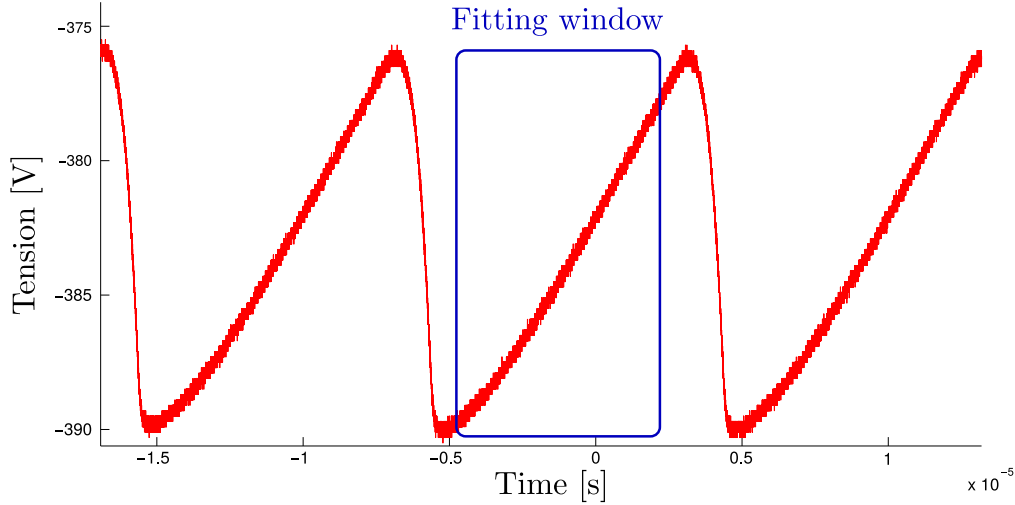


Figure 3.8: Representation of the signal approximated for the first detector. The approximation is performed on the increasing part (surrounded in blue).

apparatus. This means that both of them can be used in the final experimental set-up without any risks of signal deterioration. All the results presented hereafter were obtained with the first photomultiplier that is less sensitive than the other one and that requires less precautions for its implementation in the set-up. Owing to its high sensitivity to light, the second one has to be perfectly insulated for any source of parasite light.

3.2 Data acquisition and processing

3.2.1 Analytical model function of the signal decay

This section will briefly develop the LABVIEW routine that was designed to perform the CRDS measurements. This routine is based on a mean square approximation of the exponential decay measured by the photomultiplier located at the output of the cavity which can be generally written as in equation (3.1).

$$y(t) = A \exp\left(\frac{-t}{\tau}\right) + K \quad (3.1)$$

Where A is the amplitude, τ the decay time (in the case of CRDS it is called the ring-down time) and K the offset.

The aim of this routine is to perform a fit of the signal, that is composed of more than 60 000 points, in order to obtain an approximate exponential decay, $y^h(t)$ with the fitted parameters A_n , τ_n and K_n . This approximated signal is given by equation (3.2).

$$y^h(t) = A_n \exp\left(\frac{-t}{\tau_n}\right) + K_n \quad (3.2)$$

This signal is said to be approximated because it will not be possible to obtain an exponential that passes through all the points of the signal. Moreover, it has been demonstrated in section 1.3 that several modes of the cavity will be excited by a single pulse of the laser. This means that the signal leaked by the cavity will be the superposition of several exponential decays with different values of τ . There are several ways to obtain the best exponential; one of them consists

in minimising the residue defined by equation (3.3). The points (T_i, Y_i) are the m points present in the signal. In order to minimise this residue, it is necessary to find the values of the parameters A_n , τ_n and K_n which best fit the experimental data.

$$J(A_n, \tau_n, K_n) = \sum_{i=1}^m \left(Y_i - A_n \exp \left(\frac{-T_i}{\tau_n} \right) + K_n \right)^2 \quad (3.3)$$

The best fitting parameters are the ones which fulfil equations (3.4).

$$\begin{cases} \frac{\partial J(A_n, \tau_n, K_n)}{\partial A_n} = 0 \\ \frac{\partial J(A_n, \tau_n, K_n)}{\partial \tau_n} = 0 \\ \frac{\partial J(A_n, \tau_n, K_n)}{\partial K_n} = 0 \end{cases} \quad (3.4)$$

This system is a system of three independent equations involving three unknowns. Therefore, it accepts an unique solution. This solution, for the set of data $(T_i, Y_i) \quad \forall i = 1, 2, \dots, m$, provides the best approximation of the exponential decay of the signal at the output of the cavity.

3.2.2 General scheme of the data analysis with the Labview routine

The LABVIEW routine can be separated into three blocks. The first one (on the left of Figure 3.9) controls the operating mode of the oscilloscope used to record the signal coming from the photomultiplier. The signal is first averaged thanks to the average mode of the oscilloscope. In a second time, this averaged signal is transferred to the computer in order to be processed. This first block also controls the trigger of the oscilloscope. In our case, the measurement is triggered when the signal increased above a given threshold..

The second block of the LABVIEW routine (in the centre of Figure 3.9) is the one that sets the scene for the approximation. This part creates the time and tension vectors corresponding to the signal that has to be approximated. It also handles the cursors that determine the time window in which the fit will be made. This time window is important because it ensures that the fit will only be done on the exponential decay part and not on other parts of the signal (mainly the increasing parts and the transitions between decreasing and increasing parts) what could corrupt the obtained spectrum.

The third and last block of the routine (on the right of Figure 3.9) is the one that performs the fit. The working principle of the fit has already been detailed in section 3.2.1. Once the fit is achieved, the fitted parameter τ_n is stored in a vector and then plotted with respect to the wavelength (if one suppose that the wavelength range is continuously swept). Statistical properties of the obtained ring-down times are evaluated such as mean, variance and standard deviation. These statistical information allows among other to obtain information about the baseline of the spectrum.

More details about the LABVIEW routine are given in appendix B.

3.2.3 Validation of the Labview routine

Before being used on the experimental set-up, this routine was validated using an arbitrary waveform generator and the same oscilloscope that was used afterwards on the experimental set-up. This validation step guarantees that the routine works correctly and that no problem will be encountered during the CRDS measurements. Three different parts of the routine were verified. The first part is the control of the oscilloscope from the LABVIEW routine. The second part is the

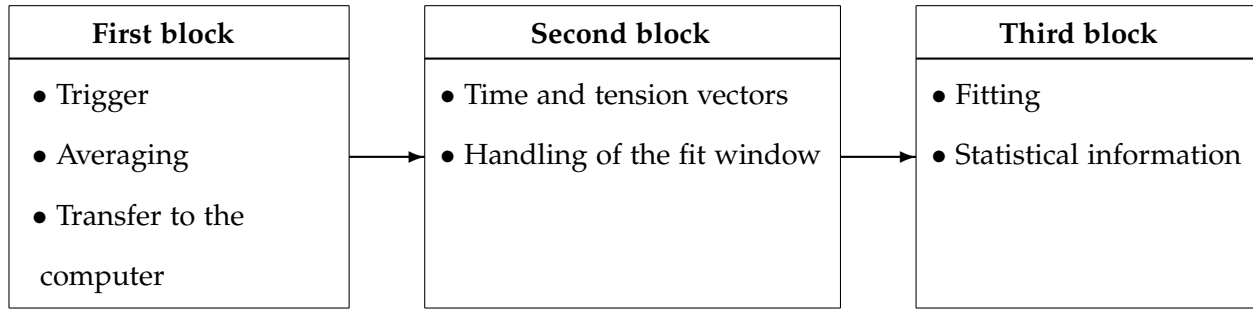


Figure 3.9: Time sequence and general scheme of the working principle of the LABVIEW routine used to perform the fit of the signal of the photomultiplier tube placed at the output of the cavity.

behaviour of the fitting window and of the approximation of the exponential decay. The last part is the validation of the fitting procedure by studying the evolution of the variance on the ring-down time with respect to the number of averaged signals. Since an exponential decay cannot be generated by the arbitrary waveform generator, another exponential signal was used. This signal is presented in Figure 3.10.

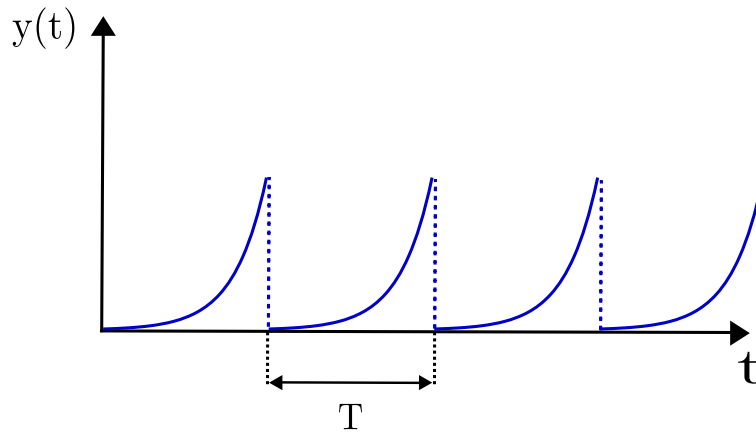


Figure 3.10: Signal generated by the arbitrary waveform generator in order to validate the LABVIEW routine. T corresponds to the period of the signal.

This signal is a periodic signal of period T composed of exponential decays whose characteristic time is $\tau \approx \frac{T}{3}$. The first two parts of the validation have been verified by the running of the routine itself whereas the third one requires further analysis of the obtained data.

To validate the fitting procedure, the evolution of the variance of the ring-down time obtained by fitting the signal, generated by the arbitrary waveform generator, has been considered. This signal had a frequency of 10 MHz which approximately corresponds to the signal at the output of the cavity. Between 2 and 1024 signals were averaged. The variance of the inverse⁴ of the characteristic time was obtained on a statistical sample of 75 signals. Figure 3.11 represents the evolution of this variance with respect to the number of signals averaged. These signals were not measured in real time but at a lower frequency defined by the number of signals averaged (this frequency ranges between 1 and 3 Hz).

⁴The variance of the characteristic time will follow the same trend as the one of its inverse.

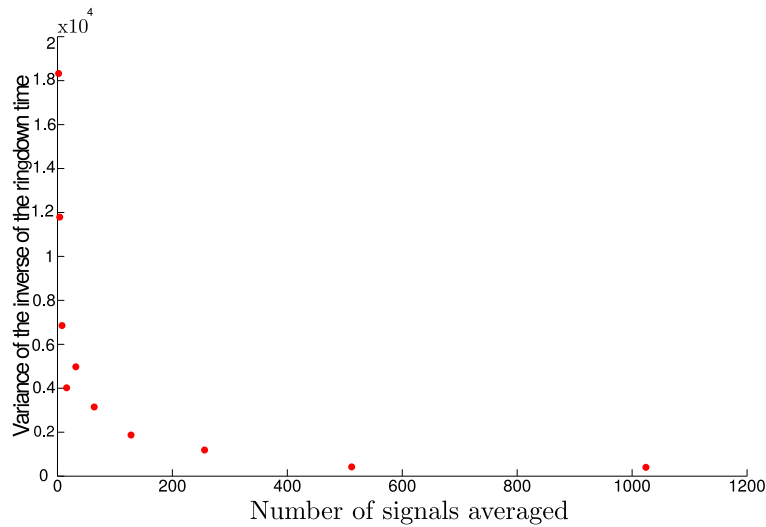


Figure 3.11: Evolution of the variance of the ring-down time of the exponential decays generated by the signal generator with respect to the number of signals averaged. The inverse of the ring-down time that has to be found is approximately $\frac{1}{\tau} = 30$ MHz which means that the variances that appear in this figure are lower than 0.1% of this value. The fit can therefore be considered as efficient.

This figure clearly shows that the value of the variance of the characteristic time of the exponential signal decreases with the number of signals averaged by the oscilloscope. This confirms the relevance of the use of the averaging inside the LABVIEW routine.

3.2.4 Improvements of the routine

Despite the results obtained (see section 3.3), the routine that has been implemented has some drawbacks. The first one is that the instrument routine scans the wavelengths at a speed that is different from the one of the laser. This can be explained by the fact that the scanning rate of the laser is perfectly known since it is given by the software that controls the laser whereas the one of the measurements is not exactly known⁵ and because there is no communication between the laser and the experimental set-up. It means that for long measurements, a slight shift in wavelengths can be observed. Two cases have to be considered, either the laser scans the frequency range faster or slower than the LABVIEW routine does. The scanning rate of the laser is defined by the working mode of the laser. This one emits x pulses at a given wavelength and then goes to the following wavelength.

This problem can be addressed by synchronising the two processes. It can be achieved with a NI-DAQ connected to the laser and to the computer. This device will send a signal to the measurement routine when the desired wavelength has been reached by the laser and then the ring-down can be measured at this wavelength. This has not been implemented yet in the LABVIEW routine because of a lack of time.

Another possible improvement of this routine is to allow to directly control the laser and the instrument routine from the same computer. The scanning speed of the laser will be controlled by the same routine as the one controlling the scanning rate for the measurements. This has not

⁵The time delay between two measurements can be chosen and thus known, however the time required to perform a single measure is not known.

been implemented yet in the LABVIEW routine because it requires advanced knowledge of the control of the laser.

This routine can also be improved by increasing the speed of the fitting procedure thanks to another algorithm (see Ref. [31]).

3.3 Experimental results

The experimental set-up and the LABVIEW routine respectively described in sections 3.1 and 3.2 allow to measure the spectrum of a gas mixture contained in the cavity. Some measurements have been performed on the air of the laboratory in two wavelength windows. The first one is a window corresponding to a vibronic transition of H_2O (between 648.5 and 650 nm) whereas the second one is a window corresponding to a vibronic transition of O_2 (between 628.15 and 631.5 nm). These two windows were separately probed and the two spectra analysed. All the measurements were performed at the laboratory temperature ($T_{\text{lab}} \approx 23^\circ\text{C}$) and ambient pressure ($p_{\text{amb}} \approx 1\text{atm}$). The first window was investigated twice and the second one only once.

3.3.1 Overtone spectrum recorded in air between 648.5 and 650 nm

This first window is supposed to correspond to a vibrational band of the H_2O molecule. The raw data directly obtained from the LABVIEW routine provides the value of the inverse of the ring-down time $1/\tau$ with respect to the wavelength λ . In order to follow the spectroscopic conventions, this spectrum will rather be expressed in terms of wavenumber. The recorded spectra are shown in Figure 3.12.

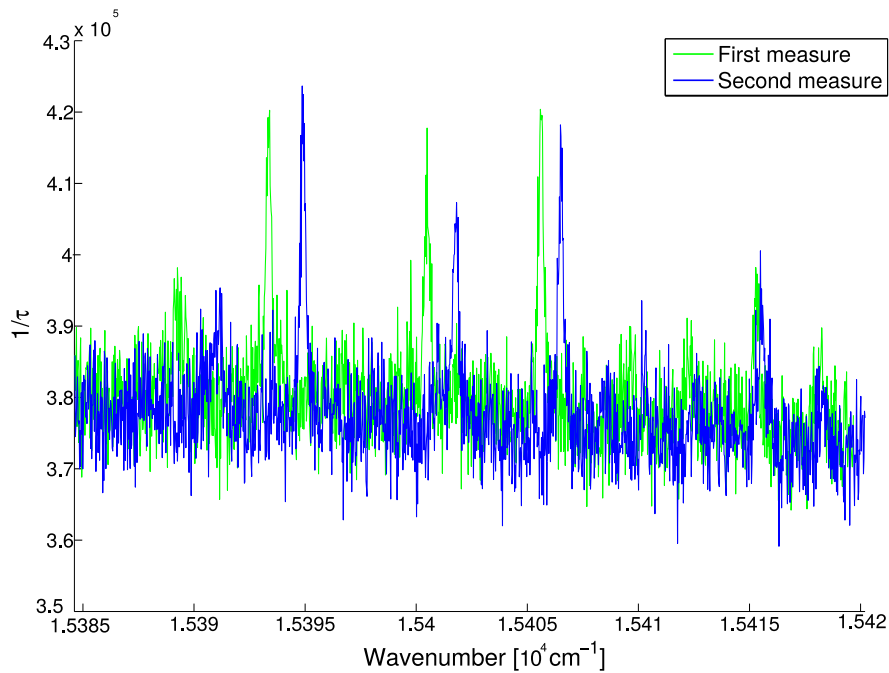


Figure 3.12: Evolution of the inverse of the ring-down time for the air in the range between 15385 and 15420 cm^{-1}

The two different colors in this figure correspond to the two measurements that were performed. It can be noticed that there is a shift between the two spectra. This shift increases from the right to the left of the figure. The measurements were started at the lowest wavelength, that

corresponds to the higher wavenumber (the right end of the figure) and were stopped at the highest wavelength that corresponds to the lowest wavenumber at the left end of the figure. The shift is due to the fact that the scanning speed of the instrumental set-up was not the same for the two measurements. The first one was performed at higher speed. The x-axis is not an absolute axis, it is defined by the LABVIEW routine and it depends on different parameters like the scanning speed or the data acquisition time by the oscilloscope.

Before going any further, it can be said that these signals are relatively noisy. This means that some lines may be hidden by the noise on the signal. In order to remove this noise, a moving average has been used. This moving average is relatively easy to implement because it considers each point of the spectrum as the mean value of itself and its two nearest neighbours. In mathematical terms it is expressed, for a vector x of length n , by (3.5).

$$x_{\text{mean}}(i) = \frac{x(i-1) + x(i) + x(i+1)}{3} \quad \forall i = 2, 3, \dots, n-2, n-1 \quad (3.5)$$

This moving average has been applied ten times and the result provides a far less noisy spectrum. The comparison between the spectrum before and after the application of this moving average is shown in Figure 3.13 for the first measurement (the result being the same for the second measurement).

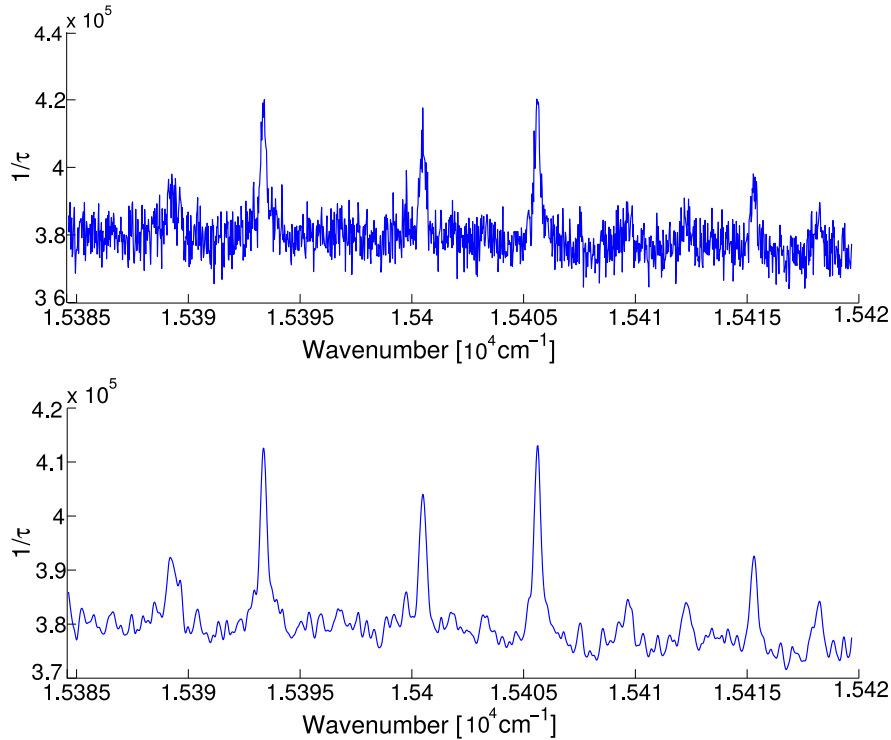


Figure 3.13: Comparison between the raw spectrum of the gas mixture (upper part) and the one obtained after applying the moving average ten times (lower part).

It could be interesting to wonder whether the application of this moving average has corrupted the spectrum or not. The signal is said to be corrupted if some lines of the spectrum are smoothed or wiped out by the moving average. In order to answer this question, it is necessary to do a frequency analysis of the signal before and after the application of this moving average. Figure 3.14 represents the fast Fourier transforms (fft) obtained for the signal before and after the

application of the moving average. The fft have been performed by using the *fft* built-in function of MATLAB which implements the fast Fourier transform algorithm.

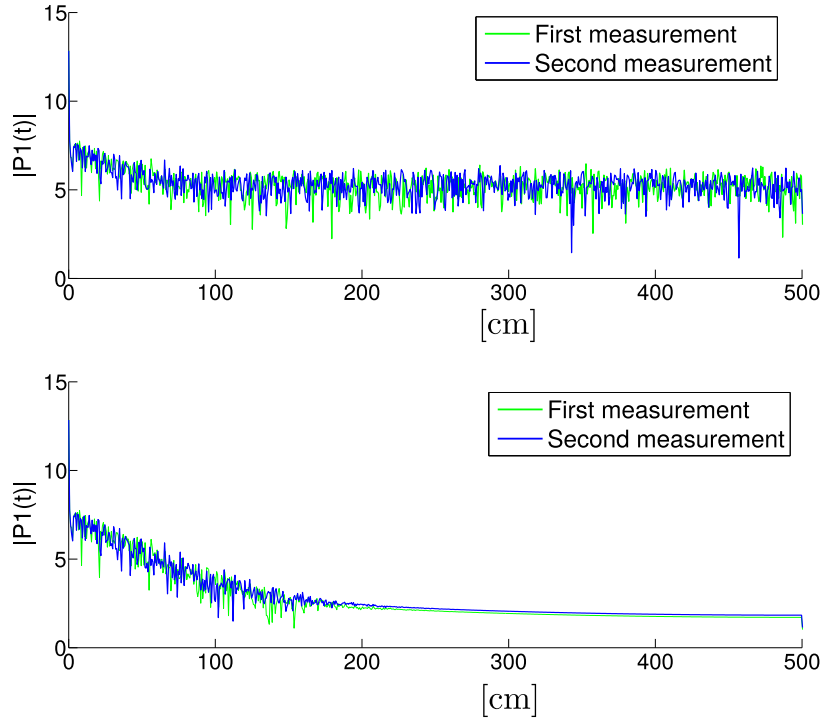


Figure 3.14: Comparison of the frequency content of the spectra before (upper part) and after (lower part) applying the Fourier transform. The frequencies axis are given in terms of $[cm]$ because the direct domain is given in $[cm^{-1}]$.

In Figure 3.14, it can be seen that the application of the ten moving averages corresponds to the application of a low pass filter. This means that only the small frequencies are conserved whereas the high frequency components tend to vanish. This is coherent with the fact that, in Figure 3.13, the noise decreases. Indeed, the noise is a high frequency signal. The question is now to determine whether the application of a low pass filter could corrupted the spectrum or not. To answer this question, it is interesting to point out that the lines in the spectrum can either have a Gaussian line shape, either a Lorentzian line shape or a Voigt line shape (that corresponds to the convolution of the two previous ones, see section 3.3.3 for more details). Moreover, the Fourier transform of a Gaussian is another Gaussian centred at the origin and the Fourier transform of a Lorentzian is an exponential decay. Thanks to the property whereby the convolution of two functions in the direct domain corresponds to their product in the frequency domain, it can be said that the Fourier transform of a Voigt line shape will mainly contain low frequency components. This means that most of the frequencies corresponding to the lines are low frequencies and then are not affected by the low-pass filter. It can be concluded that the application of the moving average does not corrupt the spectrum.

The next step consists in the transformation of the inverse of the ring-down time in terms of the absorption coefficient. In order to do this, it is necessary to express the ring-down time as in equation (1.11).

$$\frac{1}{\tau(\bar{\nu})} = \alpha(\bar{\nu})c - \frac{c(1-R)}{l} \quad (3.6)$$

Where c is the speed of light, α the absorption coefficient at the considered wavenumber, R the reflectivity of the mirrors and l the length of the cavity. The absorption coefficient can thus be expressed as a function of the ring-down time as in equation (3.7).

$$\alpha(\bar{\nu}) = \frac{1}{\tau(\bar{\nu})c} - \frac{(1-R)}{l} \quad (3.7)$$

In Figure 3.13, it can be seen that both of these spectra possess a non zero baseline. To compare them to the spectrum based on the Hitran database, it is necessary to remove this baseline. Figure 3.15 compares these two graphs with the one obtained thanks to Hitran database.

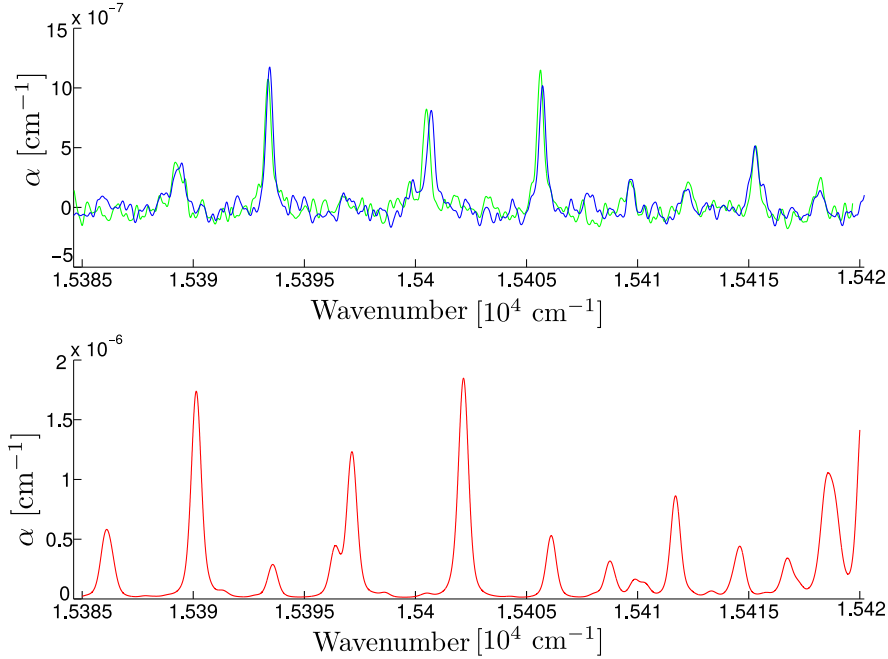


Figure 3.15: Comparison between the experimental spectrum (upper part) and the one obtained based on the Hitran database (lower part) for pure H_2O for the window between 648.5 and 650 nm. The Hitran spectrum has been obtained with Voigt line profiles for the lines and an apparatus function simulated by a Gaussian of 0.4 cm^{-1} FWHM.

In Figure 3.15, it can be seen that the two spectra (the ones obtained experimentally and the one obtained by Hitran) are shifted. This is due to the experimental concern that has already been explained: the measurement speed of the experimental set-up is not synchronised with the scanning rate of the laser. However, thanks to the relative intensities, it is possible to identify the lines and to characterise the experimental set-up.

If these the experimental spectrum is shifted in order to match the x-axis with the one of the Hitran spectrum, it is possible to compare it to the partially homemade simulation. Figure 3.16 presents these two spectra. The comparison of the experimental spectrum with the simulated one allows to say that all the lines that appear in this window correspond to the H_2O molecule.

The simulation has been upgraded compared to the one presented in section 2.4 because the obtained plot only concerns certain vibrational bands. In order to do this, one first needs to choose the transitions whose final state is one of the desired vibrational states. A selection is thus made on the values of ν_1 , ν_2 and ν_3 . As said earlier, the simulation designed in the frame of this thesis is not yet capable of computing the intensity of a given transition. In order to address this problem, the spectra that will be studied hereafter will be normalised spectra. We normalised the

spectrum in a given window by the highest value of the spectrum in this window. The obtained spectra will thus be contained between 0 and 1⁶. Figure 3.16 represents the normalised spectra obtained in the window between 648.5 and 650 nm.

The spectrum represented in the lower part of Figure 3.16 has been obtained by simulation of only one excited vibrational state $v_1v_2v_3 = 311$. This vibrational state has been chosen based on the identification of the lines made in Ref. [29]. In order to match the broadening of the simulated lines with the measured ones, it was required to convolute each line by an additional Gaussian line shape. This means that a spectral width of the source had been neglected in the simulations. This increasing of the linewidth is an effect due to the set-up and its resolution on the lines, it is called the apparatus function.

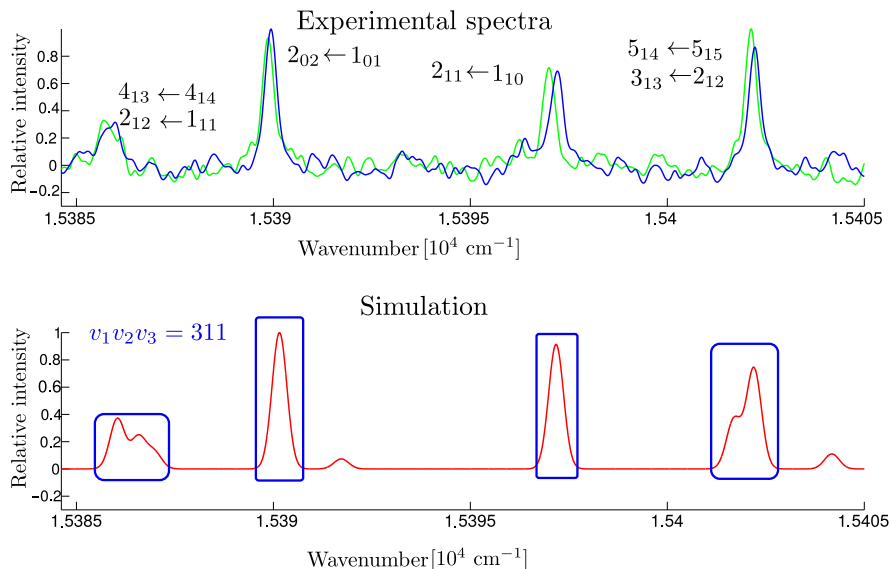


Figure 3.16: Comparison between the spectrum obtained experimentally (upper part) and the one obtained by simulation (application of equation (2.59)) for the vibrational states $v_1v_2v_3 = 311$ (lower part) at 296K. On the experimental spectrum, the transitions are assigned with the following notation $J'_{K'_aK'_c} \leftarrow J''_{K''_aK''_c}$.

3.3.2 Overtone spectrum recorded in air between 628.15 and 631.5 nm

The structure of this section is the same as the one of section 3.3.1 so only the final results will be developed. The moving average is also applicable to the raw spectrum for the same reasons than the ones detailed in section 3.3.1. The measured spectrum and the experimental spectrum obtained thanks to the Hitran database are compared in Figure 3.17.

Lots of information are contained in this experimental data. One can firstly identify the molecule and assign the transition to which each line corresponds. Secondly, the resolution and the sensitivity of the experimental set-up can be determined. The resolution is defined as the FWHM of the experimental lines whereas the sensitivity is the smallest intensity that can be detected by the experimental set-up. Thirdly, this experimental spectrum provides information about the concentration of the different molecules present in the gas mixture. It is useful to

⁶Actually, owing to the noise, some wavelengths can have a negative intensity but it however has no physical meaning.

determine for example the moisture level of this mixture or the amount of greenhouse gases in a given atmosphere. This section will go through these different analysis.

3.3.2.1 Assignment of the lines observed between 628.15 and 631.5 nm

The comparison of this experimental spectrum with the spectra of the water molecule and of the dioxygen molecule simulated by Hitran allows to say that all the lines of the experimental spectrum of Figure 3.17 correspond to transitions of the water and the dioxygen molecules.

The identification of the lines in this experimental spectrum is a little bit more tricky than the one that was performed for the first investigated wavelength window because two different molecules (O_2 and H_2O) have transitions in the considered spectral window. The experimental spectrum will firstly be compared to a simulated spectrum generated by the Hitran database for a predefined gas mixture. The composition of this gas mixture (that is the atmosphere with a given moisture level) is given in Table 3.2. The comparison between these two spectra is performed in Figure 3.17.

Gas	Molar fraction (%)
H_2O	1.19
CO_2	0.033
O_3	2.10^{-6}
N_2O	31.10^{-6}
CO	15.10^{-6}
CH_4	17.10^{-5}
O_2	20.09
N_2	77.87

Table 3.2: Composition of the gas mixture *USA model, high latitude, summer* of the Hitran database.

It can be noticed from the inspection of the Figure 3.17, and particularly from the comparison between experiment and simulation, that the intensity of some of the lines does not match exactly to one another. This is due to the fact that the composition of the atmosphere in the investigated cell is not the same as the one given in Table 3.2. Indeed, the concentration of H_2O and O_2 vary from one day to the other. The one of the water molecule will vary much more than the one of the oxygen that barely stays constant⁷. This means that the lines whose intensity is different in both spectra correspond to lines of the water molecule because the concentration of water in the atmosphere of our laboratory was not the same as the one in the gas mixture of the Hitran database. This first identification of the lines corresponding to the two molecules is approximative, there exists another method, more reliable, to identify them.

This second method consists in comparing the positions of the lines in the spectrum of the gas mixture with the ones of the simulated spectra of pure water vapour and pure dioxygen. By doing so, each line can be identified as corresponding to one molecule. This comparison is performed in Figure 3.18. In this figure, the spectrum of the gas mixture (top) is compared to the experimental spectrum (middle) and to the sum of the spectra of the H_2O and O_2 molecules (bottom) weighted in order to match, as good as possible, with the experimental spectrum. The coefficients used as weights are the molar fraction of the two gases in the gas mixture. These molar fractions are $x_{O_2} = 0.209$ and $x_{H_2O} = 0.01144$.

⁷The variation of the molar content of the water molecule in atmosphere is the order of 1-2% whereas the one of oxygen is in the order of 0.1% [32].

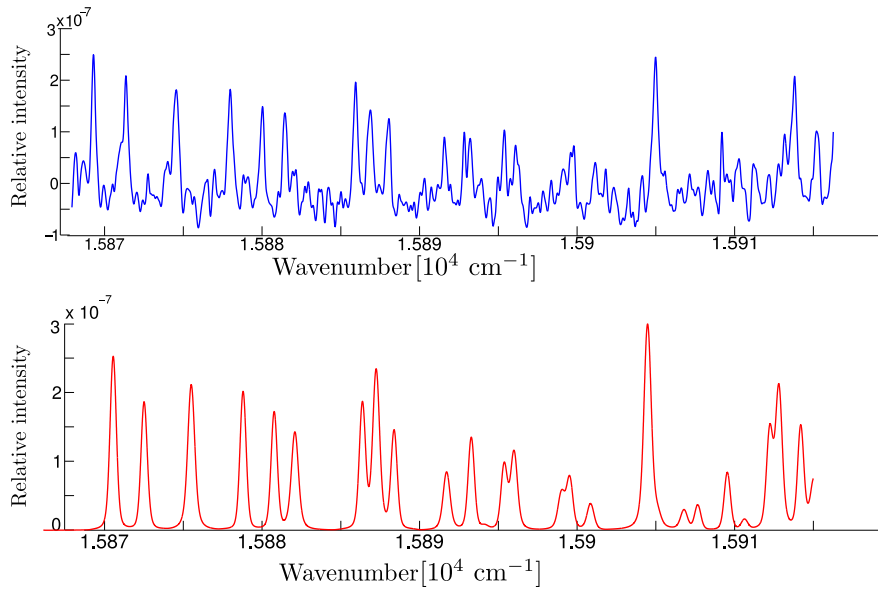


Figure 3.17: Comparison between the experimental spectrum (top) and the one obtained based on the Hitran database (bottom) for the gas mixture referred to as *USA model, high latitude, summer* in the wavelength window between 628.15 and 631.5 nm at 296K. The Hitran spectrum has been obtained with Voigt line profiles for the lines and an apparatus function simulated by a Gaussian of 0.4 [cm⁻¹] FWHM.

Now that the lines corresponding to the water molecule have been identified (the blue lines in the bottom of Figure 3.18), it is possible to identify the vibrational band to which they belong. In order to do it, the positions of the lines will be compared to the one obtained by simulation for the same wavenumber window. The wavenumber range being much higher than the one considered before, the vibrational bands concerned are different than the one found before. The identification of these vibrational bands is made in Figure 3.19. The same procedure as the one used in section 3.3.1 was used. The vibrational state of the water molecule that is identified is the $v_1v_2v_3 = 113$ state.

3.3.2.2 Characterisation of the experimental set-up

The two experimental spectra obtained in the two different windows allow to characterise the experimental set-up. Two parameters are interesting to know when performing a spectroscopic measurement. The first one is the resolution $\Delta\bar{\nu}$ that is defined by the FWHM of the experimental lines. The second one is the sensitivity α_{min} that is the intensity of the smallest line that could be detected by the set-up. These two parameters are primordial. If the resolution of the experimental set-up is too small, it will be impossible to distinguish two neighbour lines. If the sensitivity of the experimental set-up is too high, it will be impossible to distinguish a line whose intensity is small compared to the sensitivity.

These two parameters will be experimentally derived thanks to the spectra of Figures 3.15 and 3.17. In order to find the resolution, it only requires to determine the FWHM of the lines of the spectrum. The resolution of the experimental set-up is therefore $\Delta\bar{\nu} = 0.4 \text{ cm}^{-1}$. To find the sensitivity, the standard deviation of the noise have been computed and averaged on the three measurements. The sensitivity obtained this way is $\alpha_{min} \approx 5 \cdot 10^{-8} \text{ cm}^{-1}$. By comparison, the resolution obtained by O'Keefe and Deacon in Ref. [16] is $\alpha_{min} \approx 5 \cdot 10^{-9} \text{ cm}^{-1}$. This difference

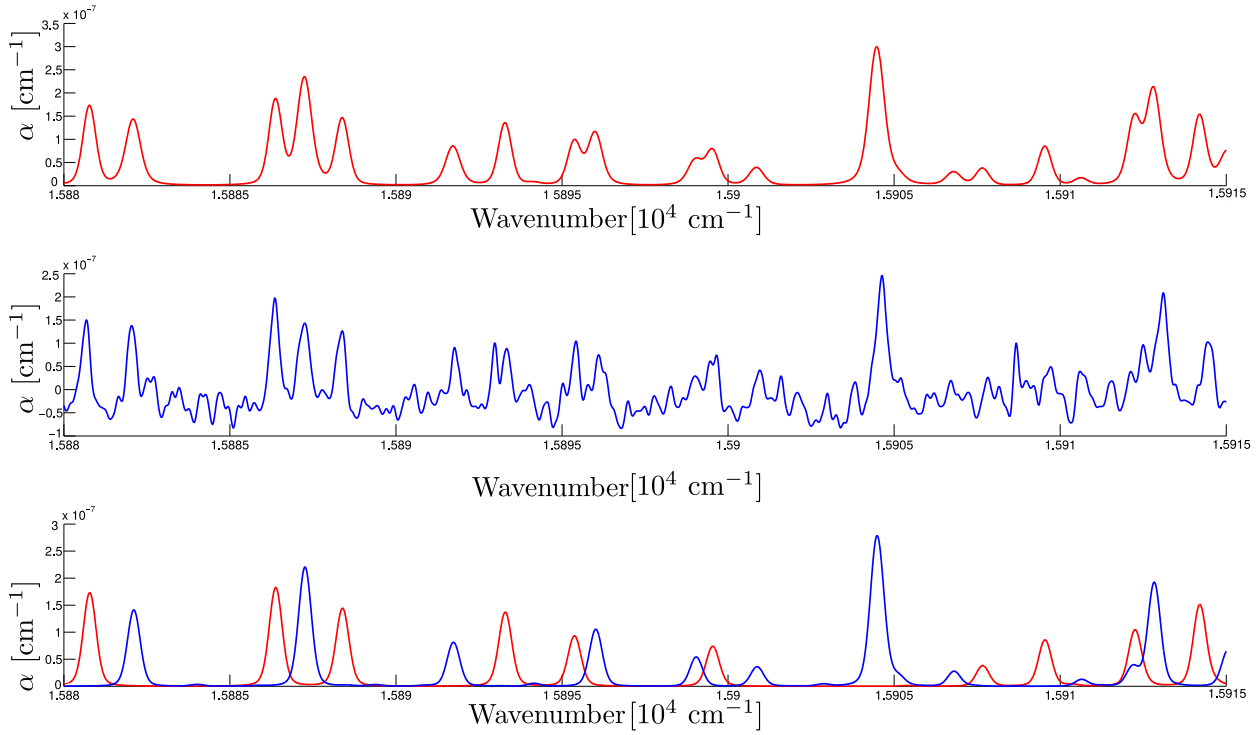


Figure 3.18: Comparison between the experimental spectrum (in the middle) with the spectrum of the *USA model, high latitude summer* gas mixture (in the top) and a weighted sum of the spectra (in the bottom) of H_2O and O_2 respectively in red and blue. All the simulations have been run at 296K.

can be explained by considering the variation of the sensitivity with respect to the ring-down time (see Ref. [33]). This variation is given by equation (3.8).

$$\alpha_{min} = (1 - R) \frac{\Delta\tau}{\tau_0} \quad (3.8)$$

The sensitivity of O’Keeffe and Deacon was obtained with ring-down times of some tens of microseconds whereas our experimental set-up gives ring-down times of some microseconds. This difference in the ring-down times (factor 10) explains the difference in the sensitivity observed between the experimental set-up detailed in this work and the one detailed in Ref. [16].

3.3.2.3 Determination of the concentration of a given molecule

The experimental spectra allow to determine the composition of the investigated gas mixture. This is due to the fact that the absorption coefficient of the gas mixture present in the cell depends on the concentration of the different gases. The absorption coefficient of the gas mixture at a given wavelength can be expressed as in equation (3.9).

$$\alpha(\lambda) = \sum_i \alpha_i(\lambda) = \sum_i \sigma_i(\lambda) n_i \quad (3.9)$$

The term $\sigma_i(\lambda)$ is the absorption cross section of the considered molecule i whereas n_i is its concentration. The absorption cross section of a molecule is independent on its concentration. This means that the absorption coefficient of a given molecule at a given wavelength is directly

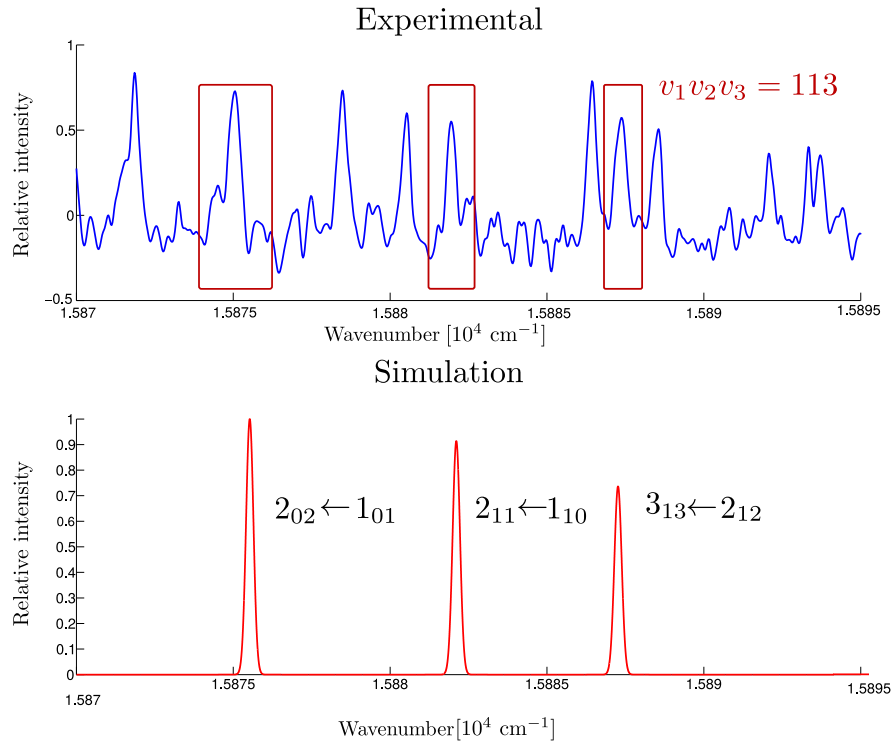


Figure 3.19: Identification of the vibrational band involved in the spectrum in a part of the window between 15860 and 15920 cm^{-1} . The top spectrum is the experimental spectrum whereas the bottom spectrum has been simulated thanks to equation (2.59).

proportional to its concentration. This property can be used to determine the moisture level of a investigated gas mixture.

The moisture level is defined as the ratio between the partial pressure of water in the considered atmosphere and temperature on the saturating vapour pressure of the water in the same temperature and pressure conditions (see equation (3.10)). The saturating vapour pressure is defined as the equilibrium pressure between a gas and its liquid. The partial pressure of a gas in a gas mixture is always smaller than the saturation vapour pressure of this gas in the same conditions.

$$\phi_{H_2O} = \frac{p_{H_2O}}{p_{H_2O}^{sat}} \quad (3.10)$$

If the gas mixture is considered as an ideal gas mixture (this means that all the gases of this mixture are considered as ideal gases), the partial pressure of a molecule i is defined by $p_i = x_i p_{tot}$ with x_i the molar fraction and p_{tot} the total pressure of the gas mixture. If the pressure and temperature are known, the moisture level can therefore be derived from the molar fraction. This molar fraction can be obtained as the multiplying factor used in for the H_2O spectrum to obtain the lower spectrum of Figure 3.18. The molar fraction of H_2O is in our case given by $x_{H_2O} \approx 0.01144$.

The last quantity that has to be introduced before obtaining the moisture level is the saturating vapour pressure of the water. Its value depends on the temperature (cfr Ref. [34]) at 23°C , the approximate temperature of the laboratory, this saturating vapour pressure is $p_{H_2O}^{sat} \approx 0.027 \text{ bar}$. The moisture level is therefore given by

$$\begin{aligned}
\phi_{H_2O} &= \frac{p_{H_2O}}{p_{H_2O}^{sat}} \\
&= \frac{x_{H_2O} p_{tot}}{p_{H_2O}^{sat}} \\
&\approx \frac{0.01144 \cdot 1.01325 \text{ bar}}{0.027 \text{ bar}} \\
&\approx 0.4294
\end{aligned}$$

This moisture level is an approximation because the values of the molar fraction of H_2O , the total pressure and the saturating vapour pressure are not exactly known. The uncertainties on these values induce an uncertainty on the value of the moisture level. Equation (3.11) gives the relation between the uncertainty on the moisture level and those of the variables on which it depends.

$$\Delta\phi_{H_2O} = \Delta x_{H_2O} \frac{p_{tot}}{p_{H_2O}^{sat}} + \Delta p_{tot} \frac{x_{H_2O}}{p_{H_2O}^{sat}} + \Delta p_{H_2O}^{sat} \frac{p_{tot} x_{H_2O}}{(p_{H_2O}^{sat})^2} \quad (3.11)$$

If one chooses the following set of values for the uncertainties : $\Delta x_{H_2O} = 0.0005$, $\Delta p_{tot} = 0.01 \text{ bar}$ and $\Delta p_{H_2O}^{sat} = 0.002 \text{ bar}$, the uncertainty on the moisture level is $\Delta\phi_{H_2O} = 0.07$.

3.3.3 Summary

The experimental set-up designed in this master thesis has been proved to be functional since spectra were recorded. These spectra were validated by comparison with the ones of the simulation and of the literature. The resolution as well as the sensitivity of this set-up have been computed and are respectively $\alpha_{min} = 5.10^{-8} \text{ cm}^{-1}$ and $\Delta\bar{\nu} \approx 0.4 \text{ cm}^{-1}$. The combination of the experimental spectra and the ones generated by the simulations allows to assign the different lines. It also permits to compute the concentration of a gas in the gas mixture.

Conclusion

This master thesis aimed at presenting both the design of a low temperature pulsed CRDS experimental set-up and the implementation of the simulation of the absorption spectrum of the water molecule in the visible range. These two objectives have been partially achieved. This conclusion will first summarise the different steps achieved and their corresponding results. If validations of these results have been performed, they will be reminded. Secondly, the considered improvements of both the simulations and the experimental set-up will be developed. Finally, this conclusion will detail the future measurements and simulations that can be performed and developed in the continuity of this master thesis.

The first chapter of this document explains the CRDS technique. At the end of this first chapter, the mode matching problem is addressed thanks to the computation of the optimal positions of the mode matching lenses. The investigated parameters are the distance between the laser and the first lens, the one between the two lenses and the one between the second lens and the input of the optical cavity of the CRDS set-up. A first way used to verify the correctness of the converged distances is to study the evolution of the width of the laser beam and its radius of curvature in the optical system with this set of distances. The obtained plots allow to assume that the distances are correct. This is however not sufficient to verify the simulation. A second way would be to mount the lenses of the mode matching on the experimental set-up and to study how they influence the intensity at the output of the optical cavity. This intensity should match with the one that could theoretically be derived from the value of the reflectivity of the mirrors. This second check has not yet been implemented since no measurement were performed with the mode matching lenses mounted on the set-up.

The second chapter of this thesis implements both the diagonalisation of the rigid rotor rotational Hamiltonian of the water molecule and the simulation of the spectrum of the same molecule. The first simulation provides the values of the rotational energy levels for the fundamental vibrational and electronic levels of the H_2O molecule. Several ways can be used to verify the validity of these values. The first one that has been implemented in this thesis consists in the study of the evolution of these values with the asymmetry parameter κ from the prolate limit to the oblate limit. This first method validates the energy levels obtained. Another way to verify these results is to compare them with the literature ([35] for example). This comparison also approves the computed energy levels. The second simulation of this chapter is the simulation of the spectrum of the water molecule based on the selection rules derived in this document. In order to be verified, the obtained spectrum has been compared with the one generated by the Hitran database for a given vibrational band (actually it was compared to reference [29]). This comparison allows to verify that the positions of the transitions are correct. The obtained

relative intensities of the lines are not correct. This simulation fuzziness is due to the fact that the computation of the intensities involves terms that were not determined in the literature and which are far too complex to be implemented in the frame of this master thesis. Nevertheless, the simulation of the spectrum allows to identify the observed lines of the experimental spectra. This simulation is used to validate the experimental spectra.

The last chapter of this master thesis displayed the results that were obtained with the experimental set-up. The first spectra obtained with this set-up show that it is operational. These spectra have been obtained without any mode matching lenses and are thus highly noisy compared to what could have been expected with these lenses. The comparison of these spectra with the ones obtained by simulation allows to identify the lines located in the investigated window and thus to compare them with the spectrum generated by the Hitran database. The experimental set-up resolution and sensitivity have been determined based on the measured spectra. A resolution of $\Delta\bar{\nu} \approx 0.4 \text{ cm}^{-1}$ and a sensitivity of $\alpha_{\min} \approx 5.10^{-8} \text{ cm}^{-1}$ have been obtained. The sensitivity of this set-up can be improved in order to perform more detailed spectral measurements.

Despite these encouraging results, both the simulations and the experimental set-up can be improved. The computation of the spectrum can be improved by developing a more detailed computation of the intensity terms. However, this may involve very time consuming subroutines and a very high computational cost because the missing terms involves the integration of energy dipole molecular surface for each transition. Another perspective of the simulation part is to extend it to other molecules, for example to the dimer of H_2O . This extension involves to take the tunnelling dynamics into account. This extension requires to redevelop the symmetry selection rules for the water dimer and to compute the energy levels of the water dimer.

The experimental set-up designed so far is relatively basic. Despite the spectrum measurements that were already made, this set-up has to be improved in order to fulfil the aim of this project. A first way to improve this set-up is to mount the mode matching lenses on the optical bench and to achieve the same measurements as previously in order to compare them. The second way to improve it, is to work at low temperature and low pressure in order to detect these multimers in conditions that are more suitable to their complexation. The set-up can also be improved thanks to the synchronisation of the scanning rate of the measurement with the one of the laser. This synchronisation requires to use a NI-DAQ device with its corresponding VI's in the LABVIEW routine. Another way to correct the x-axis scale of the spectra is to use a reference line and a Fabry Perot resonator to set a reference scale on this axis. This routine can also be improved by designing a faster computation of the exponential approximation [31] implemented in a faster language such as PYTHON or C and include it inside the LABVIEW routine.

The next few pages present a perspective for the upcoming steps of this project. The computation of the temperature profile inside a cryogenic cell is developed. This simulation will allow to determine an approximation of the temperature profile inside the cell to insert it in further simulations of low temperature spectra. A photography of this cell is finally shown.

Simulation of the homogeneity of the temperature profile in a cylindrical cryogenic cell.

One of the goals of this master thesis was to design a cryogenic cell. It will allow to study gases at low temperature and to compare the obtained spectra with the ones obtained at higher temperature in order to ease the assignment of vibrational levels and to study the partial aggregation of molecules in order to determine to what extent the temperature affects the spectrum. This section presents the geometrical description of the cell as well as the simulation that has been run in order to compute the mean temperature obtained in the designed cell. This section ends with a brief description of the influence of the temperature on the line shape of the lines of a given spectrum.

Geometrical description of the cell

The geometry of the cell designed is based on the one described by Samir Kassi in Reference [13]. The cell is composed of three concentric cylinders ①, ② and ③ of respective radii r_1 , r_2 and r_3 as illustrated in Figure 3.20. The cylinder ①, represented in red in Figure 3.20, is the chamber in which the studied gas will be injected. Since the pressure inside this chamber will be different to the one of the intermediate cylinder ②, the chamber has to be designed in order to avoid gas leak between cylinders ① and ②. The intermediate cylinder, represented in green in Figure 3.20 contains the liquid nitrogen used to cool down the gas inside the inner cylinder. It also has to be insulated from the external surrounding to avoid vaporisation of the liquid nitrogen. The outer cylinder, represented in blue in Figure 3.20, is a thermal shield that insulate the cylinder of liquid nitrogen from the outside surrounding in order to lower the amount of $N_2^{(l)}$ consumed by the system. This outer cylinder is pumped down at very low pressure in order to avoid any convection phenomenon.

The chamber in which the gas will be injected is the inner cylinder. This cylinder has a length L and a diameter $D = 2r_1$ both expressed in meters. This cylinder is not totally immersed in the liquid nitrogen cylinder because its ends have to be in contact with the cavity mirrors that cannot be in contact with liquid nitrogen for mechanical concerns. The considered cylinder is supposed to be perfectly cylindrical so that the problem can only be solved on a rectangular domain (see Figure 3.21) because of the symmetry around the longitudinal axis. This strong reduction of the spatial extent of the domain can be done because the conditions at the border of the cylinder are totally symmetric too. The rotation around the longitudinal axis of the rectangle will provide the temperature profile in the whole cylinder. The x-axis will be defined as any radial axis of the

section of the cylinder, the z -axis will be parallel to the longitudinal axis of the cylinder whereas the y -axis, that will not be used hereafter, is orthogonal to both other axis.

This geometrical description of the cell eases the expression of the boundaries conditions as well as the one of the heat transfer equation of the gas inside the inner cylinder.

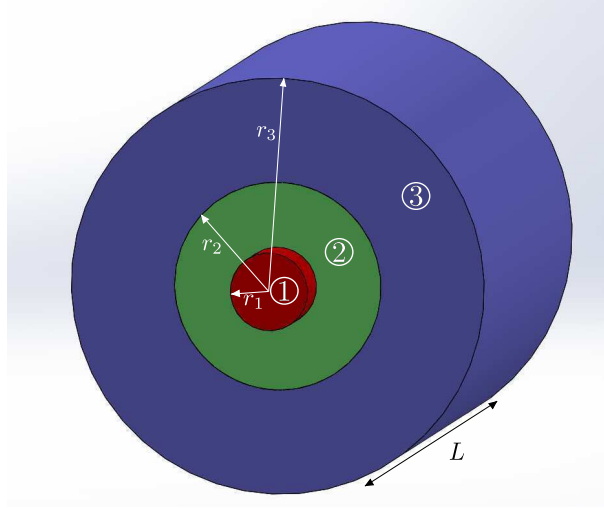


Figure 3.20: Schematic representation of the cryogenic cell composed of three concentric cylinders of respective radii r_1 , r_2 and r_3 . The red cylinder is the chamber that contains the studied gas, the green cylinder is the one that contains the liquid nitrogen and the blue cylinder is a shield that allows to reduce the loss of heat of the chamber.

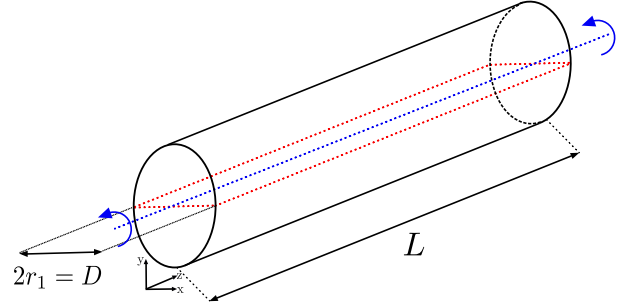


Figure 3.21: Schematic representation of the restricted domain on which the problem will be solved (in red dashed line). The axis along which the rotation of this rectangle could be performed in order to represent the temperature in the whole volume is also represented (in blue dashed line). Only the inner cylinder, of radius r_1 , is represented in this figure.

Resolution of the heat transfer equation

The resolution of the heat transfer equation inside the cell is a partial derivatives equation. Such an equation requires boundary conditions in order to guarantee the uniqueness of its solution.

Boundary conditions of the problem

Since the considered domain is a rectangle, it has only four boundaries corresponding to its four sides. A boundary condition will be applied on each of these boundaries in order to guarantee the uniqueness of the solution found. Two types of boundary conditions will be applied on them. The first ones are the conditions on the boundaries in contact with the liquid nitrogen sink, the upper and lower sides of the rectangle. These conditions only impose the temperature, $T(x, z)$, on the boundary, they are called *Dirichlet* conditions[36] and are given in equation (3.12).

$$\begin{cases} T(0, z) = 77\text{K} \\ T(D, z) = 77\text{K} \end{cases} \quad (3.12)$$

The second type of boundary conditions are the conditions set on the small sides of the rectangle. In this case, we can neither quantify the temperature, nor the heat flux at the boundary. However, the heat flux at these boundaries is equal to the one that can be evacuated by the

ambient atmosphere. This condition is called a *Robin*[36] condition. It is a mixed boundary condition because it involves both the value of the temperature and its derivative at a given point. This condition applied at the right side boundary can be written as

$$\begin{cases} \lambda_h \frac{\partial T(x, 0)}{\partial z} = -H (T(x, 0) - T_{amb}) \\ \lambda_h \frac{\partial T(x, L)}{\partial z} = H (T(x, L) - T_{amb}) \end{cases} \quad (3.13)$$

where λ_h is the heat transfer coefficient, H is the convection coefficient of the fluid in contact with the left and right sides of the rectangle. The term T_{amb} is the temperature of the fluid that is in contact with the ends of the cylinder. If this one is totally immersed inside liquid nitrogen, the temperature will be the one of the liquid nitrogen.

The most intense heat transfer phenomenon inside the inner cylinder is the conduction because the pressure is supposed to be low enough to avoid convection phenomena[13]. The heat flux inside the ambient atmosphere is controlled by the convection phenomenon.

This equation (3.13) involves partial derivatives that will be tough to handle numerically. This problem can be tackled by using a finite difference scheme of the second order⁸. This scheme allows to express the derivative as the difference between two adjacent temperature values, it is given by equation (3.14).

$$\frac{\partial T(x, L)}{\partial z} \approx \frac{T(x, L) - T(x, L - dz)}{dz} \quad (3.14)$$

The same development can be applied to the left side boundary condition. The finite difference scheme used at this second boundary is given by (3.15).

$$\frac{\partial T(x, 0)}{\partial z} \approx \frac{T(x, 0) - T(x, dz)}{dz} \quad (3.15)$$

So both *Robin* boundary conditions can be expressed in terms of finite difference schemes as follows.

$$\begin{cases} \lambda_h \frac{T(x, L) - T(x, L - dz)}{dz} \approx H (T(x, L) - T_{amb}) \\ \lambda_h \frac{T(x, 0) - T(x, dz)}{dz} \approx -H (T(x, 0) - T_{amb}) \end{cases} \quad (3.16)$$

The four boundary conditions have now been developed, they can be represented on a scheme of the domain on which the heat transfer equation will be solved, see Figure 3.22.

The heat transfer equation

In order to find the temperature profile, the local form of heat transfer equation (3.17) will be solved[36].

$$\text{div} (\lambda_h \nabla T) + P(M, t) = c_p \rho \frac{\partial T}{\partial t} \quad (3.17)$$

This equation involves several parameters that characterise the medium for which the temperature profile is computed. λ_h is the heat transfer coefficient, it characterises the ability of the medium to transfer heat by conduction, it is expressed in $[W/(m^2K)]$. $P(M, t)$ is the thermal

⁸The order refers to the dependence of the error on the discretisation step (here dz). In this case, the error on the real value of the derivative is proportional to the square of this discretisation step.

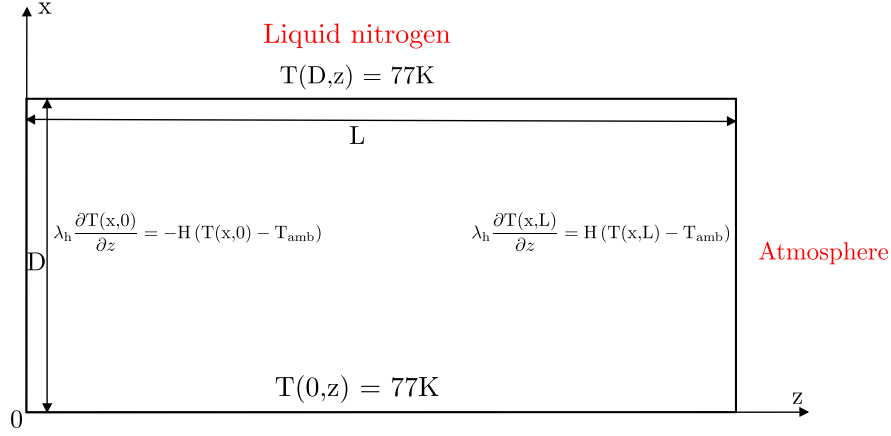


Figure 3.22: Boundary conditions on the considered domain

power dissipated in the medium (supposed equal to zero in the problem considered because the heat induced by the gas is negligible when equilibrium temperature is reached), c_p [kJ/K mol] is the heat capacity, it characterises the amount of energy needed to increase the temperature of one mole of matter of 1°C and ρ is its density expressed in [kg/m³].

Since the thermal conductivity of the gas in the cell is assumed to be isotropic, the heat transfer coefficient is not concerned by the divergence operator. One thus can rewrite the first term of (3.17) as follows:

$$\begin{aligned}
 \text{div}(\lambda_h \nabla T) &= \lambda_h \text{div}(\nabla T) \\
 &= \lambda_h \text{div}\left(\frac{\partial T}{\partial x}, \frac{\partial T}{\partial y}, \frac{\partial T}{\partial z}\right) \\
 &= \lambda_h \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) \\
 &= \lambda_h \Delta T
 \end{aligned}$$

The operator Δ is the Laplacian operator, it corresponds to the sum of the second derivatives of the temperature along the x , y and z axis, the later being not considered here because the reduced problem has only two dimensions.

The local form of heat transfer equation for the considered problem can thus be written as (3.18).

$$\rho c_p \frac{\partial T}{\partial t} = \lambda_h \Delta T \quad (3.18)$$

This local form of the heat transfer equation can also be written by developing the Laplacian operator

$$\rho c_p \frac{\partial T}{\partial t} = \lambda_h \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial z^2}\right) \quad (3.19)$$

Once again, the partial derivatives have to be replaced by a finite difference scheme in order to solve this problem. The finite difference scheme is given in equation (3.20).

$$\left\{ \begin{array}{l} \frac{\partial T(x, z, t)}{\partial t} \approx \frac{T(x, z, t) - T(x, z, t - 1)}{dt} \\ \frac{\partial^2 T(x, z, t)}{\partial x^2} \approx \frac{T(x + dx, z, t) - 2T(x, z, t) + T(x - dx, z, t)}{dx^2} \\ \frac{\partial^2 T(x, z, t)}{\partial z^2} \approx \frac{T(x, z + dz, t) - 2T(x, z, t) + T(x, z - dz, t)}{dz^2} \end{array} \right. \quad (3.20)$$

Stationary resolution

The quantity of interest is the final temperature profile inside the cryogenic cell. From a mathematical point of view, the stationary solution corresponds to the solution $T(x, z)$ obtained when $\frac{\partial T}{\partial t} = 0$. By cancelling the time derivative in equation (3.19), the stationary solution of the heat transfer equation can be obtained, it is given by equation (3.21).

$$0 = \frac{\partial^2 T(x, z)}{\partial x^2} + \frac{\partial^2 T(x, z)}{\partial z^2} \quad (3.21)$$

If all the partial derivatives appearing in this equation are replaced by their corresponding finite difference schemes, the equation obtained can be numerically solved by an iterative method. The heat transfer equation expressed in terms of these finite difference schemes is given by equation (3.22).

$$T(x, z, t) = \frac{dx^2 dz^2}{2dz^2 + 2dx^2} \left(\frac{T(x + dx, z, t) + T(x - dx, z, t)}{dx^2} + \frac{T(x, z + dz, t) + T(x, z - dz, t)}{dz^2} \right) \quad (3.22)$$

Figure 3.23 is a schematic representation of the working principle of the routine designed to compute the temperature profile in the cylindrical cryogenic cell. The first block in this figure represents the preliminary settings that have to be done before running the routine. It is necessary to define the mesh on which the heat transfer equation will be solved. Both the heat transfer equation and the boundary conditions have to be expressed in terms of the finite difference scheme in order to be numerically handled.

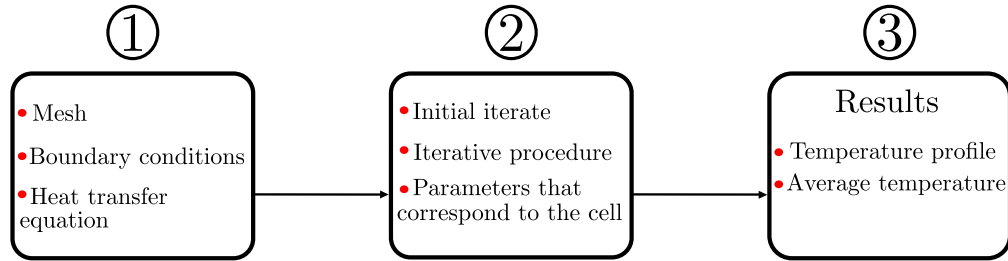


Figure 3.23: Schematic representation of the working principle of the resolution of the heat transfer equation.

In order to find the stationary temperature profile, an iterative procedure will be used. At first, one considers that all the points have an initial temperature given by T_{ext} , that is supposed to be uniform in the whole cell. Then the boundary conditions derived above will be imposed and several iterations will be run until the stationary temperature profile is reached. At each iteration, the temperature of a given point is obtained thanks to the values of the temperature of

its neighbouring points at the previous iteration. To define the boundary conditions completely, it is necessary to replace the heat transfer coefficient, λ_h and the convection coefficient H by numerical values. By using respectively $30 \text{ W}/(\text{m}^2 \text{ K})$ and $0.0454 \text{ W}/(\text{m K})$ [37] for the convection and heat transfer coefficient, the temperature profile represented in Figure 3.24 is obtained. The values of λ_h and H respectively correspond to the heat transfer coefficient of air at this pressure and temperature and to the convection coefficient of air at ambient temperature.

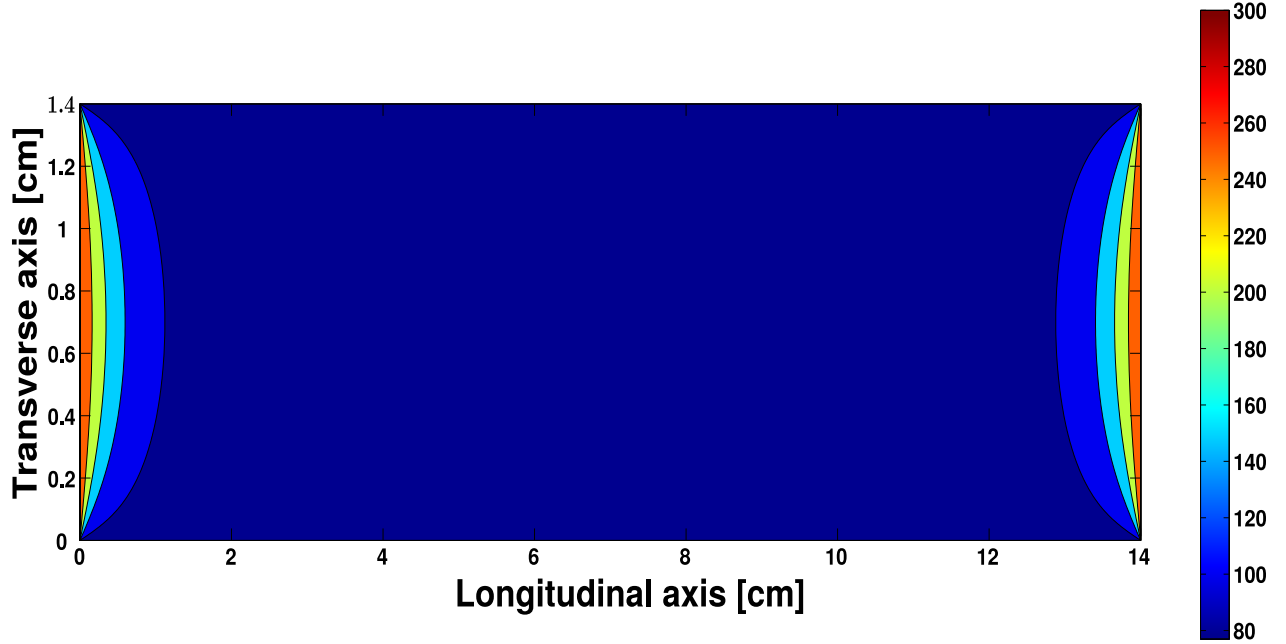


Figure 3.24: Stationary temperature profile obtained for the parameters set to $H=30 \text{ W}/\text{m}^2\text{K}$ and $\lambda_h=0.0454 \text{ W}/\text{m K}$.

In Figure 3.24, the different colours correspond to different temperature ranges, the colour scale is placed at the right side of Figure 3.24. The blue colour corresponds to positions where the temperature is low ($\approx 77\text{K}$) whereas the red/orange colour corresponds to positions where the temperature is high and close to the ambient one ($\approx 300\text{K}$). Owing to the geometry of the cell (a long thin cylinder), one can note that the temperature is low compared to the ambient temperature almost everywhere except to the left and right sides where it is closer to ambient temperature. This is due to the fact that the longitudinal axis of the cell is much longer than the transverse axis which means that the main boundary conditions will be the one applied along the longitudinal axis.

It can be interesting to know the average temperature of the cell, for example to determine the Doppler broadening (see section 3.3.3) of the molecular spectrum of a given gas. It would not be possible to measure the real temperature at each point of the cell but an average temperature can be numerically obtained thanks to the simulation that gave rise to Figure 3.24. In the case presented in Figure 3.24, the average temperature can be obtained by computing the mean value of the temperatures in the different places of the cell. One finds:

$$T_{average} = 79 \text{ K} \quad (3.23)$$

Which is slightly higher than the liquid nitrogen temperature, it can be explained by the fact that the two extremities of the cell are at room temperature. In the rest of the investigations about the Doppler broadening, the whole cell will be considered to be at this average temperature.

This average temperature can be compared to the mean value of the temperature obtained in a cylindrical cryogenic cell of the same dimensions by S. Kassi in References [13] and [14]. The temperatures obtained in these two references are close to the one obtained by simulation. It means that the designed simulation can be considered as reliable.

Influence of the temperature on the molecular spectrum

Natural broadening

The broadening of the lines present in the molecular absorption spectrum of a given molecule gives information on the natural lifetime of the excited state corresponding to the line as well as the temperature at which the molecule was probed.

The natural lifetime broadening is due to the lifetime of the excited state corresponding to the considered line. Each line in the molecular spectrum corresponds to a transition between two rovibronic molecular states. Let the lifetime of the excited state be τ_{sp} and the rate of spontaneous emission be $\Gamma = \frac{1}{\tau_{sp}}$, the Lorentzian line shape function due to the natural lifetime broadening is given by (3.24)[38].

$$g(\nu - \nu_0) = \frac{\Gamma}{(\Gamma/2)^2 + (2\pi)^2 (\nu - \nu_0)^2} \quad (3.24)$$

The width of the lines appearing in the molecular spectrum will be measured at the half maximum of the value of the line and will be called FWHM (full width at half maximum). In the case of the natural linewidth broadening, one has

$$\Delta\nu_0 = \frac{\Gamma}{2\pi} = \frac{1}{2\pi\tau_{sp}} \quad (3.25)$$

The broadening due to natural lifetime of the excited state is thus said to be an homogeneous broadening because the FWHM does not depend on the speed of the molecules, all the identical molecules will have the same lifetime broadening.

Doppler broadening

When a gas is at a certain temperature, the molecules will have a speed distribution described by the Maxwell-Boltzmann's distribution (equation (3.26)). This distribution depends on the temperature T of the gas and its molecular mass m .

$$p_u du = \left(\frac{m}{2\pi kT} \right)^{1/2} \exp \left(\frac{-mu^2}{2kT} \right) du \quad (3.26)$$

The corresponding line shape function can be obtained by using a change of variables between the speed u and the frequency ν . Let us consider the Doppler effect of a frequency ν_0 when the transmitter moves at a speed u . The measured frequency is given by (3.27).

$$\nu = \nu_0 \left(1 + \frac{u}{c} \right) \quad (3.27)$$

It is thus possible to derive expressions of u and du as functions of ν , ν_0 and c . One respectively has

$$\begin{cases} u = \frac{c(\nu - \nu_0)}{\nu_0} \\ du = \frac{c d\nu}{\nu_0} \end{cases} \quad (3.28)$$

Equation (3.26) can therefore be expressed in terms of frequency only

$$p_\nu d\nu = \frac{1}{\nu_0} \left(\frac{mc^2}{2\pi kT} \right)^{1/2} \exp \left(\frac{-mc^2 (\nu - \nu_0)^2}{2kT\nu_0^2} \right) d\nu \quad (3.29)$$

The obtained line shape function is thus by equation (3.30).

$$g_D (\nu - \nu_0) = \frac{1}{\nu_0} \left(\frac{mc^2}{2\pi kT} \right)^{1/2} \exp \left(\frac{-mc^2 (\nu - \nu_0)^2}{2kT\nu_0^2} \right) \quad (3.30)$$

This line shape function being a Gaussian, the corresponding FWHM is given by equation (3.31) and equation (3.32) respectively expressed in terms of frequency and wavenumber.

$$\Delta\nu_D = 2\nu_0 \sqrt{\frac{2kT \log(2)}{mc^2}} \quad [\text{Hz}] \quad (3.31)$$

$$\Delta\bar{\nu}_D = 7.1 \cdot 10^{-7} \bar{\nu}_0 \sqrt{\frac{T}{M}} \quad [\text{cm}^{-1}] \quad (3.32)$$

In this case, the broadening of the line is said to be inhomogeneous because it depends on the speed of the molecules. Two identical molecules can therefore present different broadening as long as they have different speeds.

The global line shape function of a line will be the convolution between the line shape function due to the natural lifetime of the excited state (which is a Lorentzian function) with the line shape function due to the speed distribution (which is a Gaussian function). The obtained line shape function is called a Voigt function.

The Voigt profile and the measurement of temperature

The convolution of the Lorentzian line shape function due to natural lifetime with the Gaussian line shape function due to Doppler broadening will give rise to a Voigt line shape function. Let f_L and f_G respectively be the FWHM of the Lorentzian and Gaussian functions. The FWHM of the convolution of these two functions can be expressed as in equation (3.33).

$$f_V \approx f_G \left(1 - c_0 c_1 + \sqrt{\phi^2 + 2c_1 \phi + c_0^2 c_1^2} \right) \quad (3.33)$$

Where $\phi = \frac{f_L}{f_G}$, $c_0 = 2.0056$ and $c_1 = 1.0593$ are parameters that have been experimentally determined [38].

Let assume that the natural lifetime and thus the FWHM of the Lorentzian line shape function f_L is known. The measure of the spectrum at a given temperature will determine the broadening (in terms of frequencies) of all the lines present in the spectrum. By using equations (3.33) and (3.30) as well as the value of f_L , it is possible to measure the average temperature of the probed gas.

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Reminder of group theory

The development and concepts presented in this section are inspired from [39], [40] and [23]. In order to determine the symmetry of the H_2O wavefunction, it will be useful to introduce some notions of group theory. Group theory is a mathematical theory used in molecular physics to ease the evaluation of the molecular Hamiltonian as well as the determination of the selection rules.

A.1 Definitions

A *group* is defined as a set of elements (in this thesis the elements of the group will be operators that can be written as vectors or matrices) that fulfils the following four rules [23].

- "The product of two elements of the group and the square of each element must be an element of the group. The product between two elements of the group has thus to be defined".
- "There must be an element in the group that commutes with all the other ones and leave them unchanged. This element is said to be the neutral element".
- "The product between elements of the group is associative. This can be expressed"

$$(AB)C = A(BC) \tag{A.1}$$

- "Each element R of the group must have a reciprocal R^{-1} , that is also in the group, such that $RR^{-1} = E$ where E is the neutral element of the group."

A *class* is a subset of a group whose elements are linked to one another by *similarity transformations*. If A and B are two elements of a group, then $B^{-1}AB$ will be equal to C that is also in the group. C is said to be the similarity transform of A by B .

A.2 Representation of groups

In the following, the elements of the considered group will be symmetry operators. Let $\mathcal{G}$ be the group of these operators that act on a vector space $\mathcal{L}$. We would like to study the representation of G that is the group of the symmetry operations. Each symmetry operation R can be represented by a matrix $D(R) \in \mathcal{G}$ that depends on the chosen basis set used for the representation.

The following homomorphism¹ between the group G of the operations and the group $\mathcal{G}$ of the operators can be defined

$$\begin{aligned} G &\longrightarrow \mathcal{G} \\ R &\longrightarrow D(R) \\ RS &\longrightarrow D(R)D(S) \\ R^{-1} &\longrightarrow D(R^{-1}) = (D(R))^{-1} \\ E &\longrightarrow D(E) = \mathbb{1} \end{aligned}$$

Moreover, the homomorphism between the groups G and $\mathcal{G}$ is an isomorphism because there is a one to one relation between the elements of G and the ones of $\mathcal{G}$.

The group G is a group of symmetry operations whereas the group $\mathcal{G}$ is the group of the representations of these symmetry operations as matrices. The combination of these symmetry operations can be represented as a usual matrix product. The neutral element of the group G , E , is represented by a $n \times n$ identity matrix where n is the dimension of the vector space $\mathcal{L}$.

Let $f = \{f_1, f_2, \dots, f_n\}$ be a basis set of $\mathcal{L}$, the action of the symmetry operation represented by $D(R)$ on an element f_i of this basis set can be written

$$D(R)f_i = \sum_j D_{ij}^f(R)f_j \quad (\text{A.2})$$

where $D^f(R)$ is the operator of R expressed in the f basis set.

Let us now consider the case where the operation R is applied after the operation S on the same element f_i .

$$\begin{aligned} D(R)D(S)f_i &= D(R) \sum_j D_{ij}^f(S)f_j \\ &= \sum_i D_{ki}^f(R) \sum_j D_{ij}^f(S)f_j \end{aligned}$$

One can thus define the representation of the product of the operations R and S as a matrix product as given in the third relation of the homomorphism.

$$\underline{\underline{D}}^f(RS) = \underline{\underline{D}}^f(R) \cdot \underline{\underline{D}}^f(S) \quad (\text{A.3})$$

If the basis set of the representation of the symmetry operation changes, the corresponding representation will be changed as follows

$$\underline{\underline{D}}^g(R) = \underline{\underline{A}} \cdot \underline{\underline{D}}^f(R) \cdot \underline{\underline{A}}^{-1} \quad (\text{A.4})$$

where $\underline{\underline{A}}$ is the transformation matrix that sends $\{f\}$ on $\{g\}$. This will give rise to a second representation of the symmetry operation R . By extension, it can be said that, for each symmetry operation, there exists an infinity of representations².

Two representations of a group G are said to be *equivalent* if there exists a matrix $\underline{\underline{A}}$ invertible such that (A.4) holds for all operations in G .

Moreover, one can define the character of a symmetry operation $\chi(R)$ as the trace of its representation.

¹ An homomorphism is a relation between two different groups.

² Each of them will be expressed in a different basis set of the vector space $\mathcal{L}$.

$$\chi(R) = \sum_i D_{ii}^f(R) = \text{Tr } \underline{\underline{D}}^f(R) \quad (\text{A.5})$$

Two equivalent representations have the same character.

One can now define an *equivalence class* as being the subset of the symmetry operations of the group that possess the same characters in a given representation.

A.3 Irreducible representations and theorems

A representation Γ of a group G is said to be reducible if there exists an orthogonal basis set such that all the matrices $\underline{\underline{D}}(R)$ for all elements R of G can be written as follows

$$\underline{\underline{D}}(R) = \begin{bmatrix} \underline{\underline{D}}'(R) & 0 \\ 0 & \underline{\underline{D}}''(R) \end{bmatrix} \quad (\text{A.6})$$

The representation Γ can thus be written as $\Gamma = \Gamma' \oplus \Gamma''$. Any representation Γ , which is said to be reducible, can be expressed as a ponderate sum of irreducible representations

$$\Gamma = \sum_i a_i \Gamma_i \quad (\text{A.7})$$

where a_i is the times the irreducible representation Γ_i is contained in Γ .

Now that the notions of characters, irreducible representations and equivalent classes have been defined, the *character table* can be introduced. It is a square table that gives the character of each equivalent class of a given group G in its different irreducible representations. It is expressed as in Table A.1.

G	$g_1\kappa_1$	$g_2\kappa_2$	$\dots$	$g_{nc}\kappa_{nc}$
Γ^1	χ_1^1	χ_2^1	$\dots$	χ_{nc}^1
Γ^2	χ_1^2	χ_2^2	$\dots$	χ_{nc}^2
$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
Γ^r	χ_1^r	χ_2^r	$\dots$	χ_{nc}^r

Table A.1: General form of a character table of a given group G . nc is the number of equivalent classes, r is the number of irreducible representations and g_i is the number of elements of the group G contained in the equivalent class κ_i .

Such a table fulfils some properties

- The number of classes (nc) is equal to the number of irreducible representations.
- $\sum_i n_i^2 = g$ which means that the sum over the square of the dimension of the representations is equal to the order of the group, defined as the number of elements in the group.
- $\sum_{c=1}^{nc} g_c \bar{\chi}_c^\mu \chi_c^\nu = g \delta_{\mu\nu}$ which is known as the *great orthogonality theorem*.
- $\sum_\nu \bar{\chi}_{c_j}^\nu \chi_{c_i}^\nu = \frac{g}{g_{c_j}} \delta_{c_i c_j}$ which is known as the *little orthogonality theorem*

Detailed description of the Labview routine

B.1 Front panel

This appendix presents the different components of the LABVIEW routine that has been designed during this master thesis. This routine performs data acquisition and data treatment from the oscilloscope connected to the photomultiplier located at the output of the optical cavity. This routine is composed of three main parts, the first one controls the data acquisition operated by the Keysight oscilloscope¹. The second part controls the cursors and the time section on which the fit has to be performed. It initialises the fit. The third part performs the fit itself.

Figures B.1 and B.2 represents the front panel of the routine.

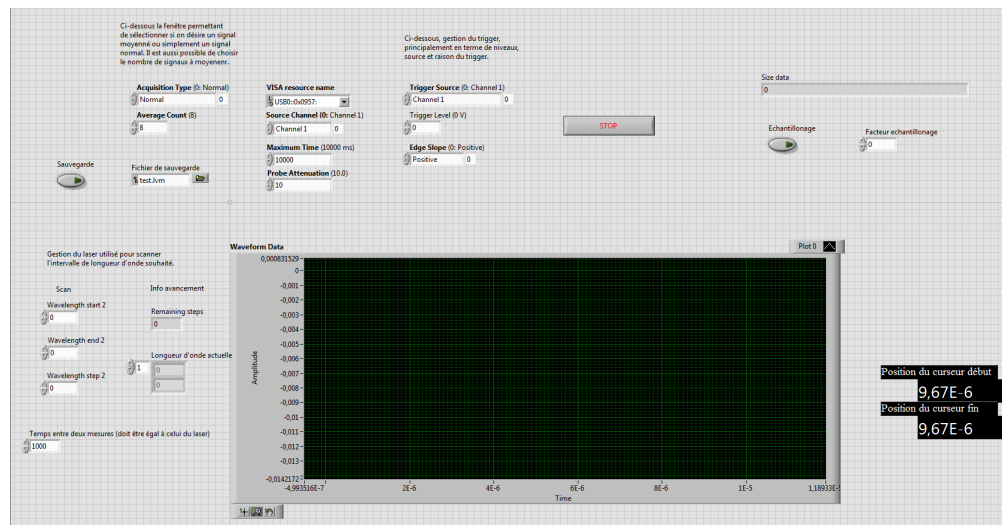


Figure B.1: Upper part of the front panel

¹For now, it is designed to work with a given oscilloscope but it can be easily adapted to other oscilloscopes

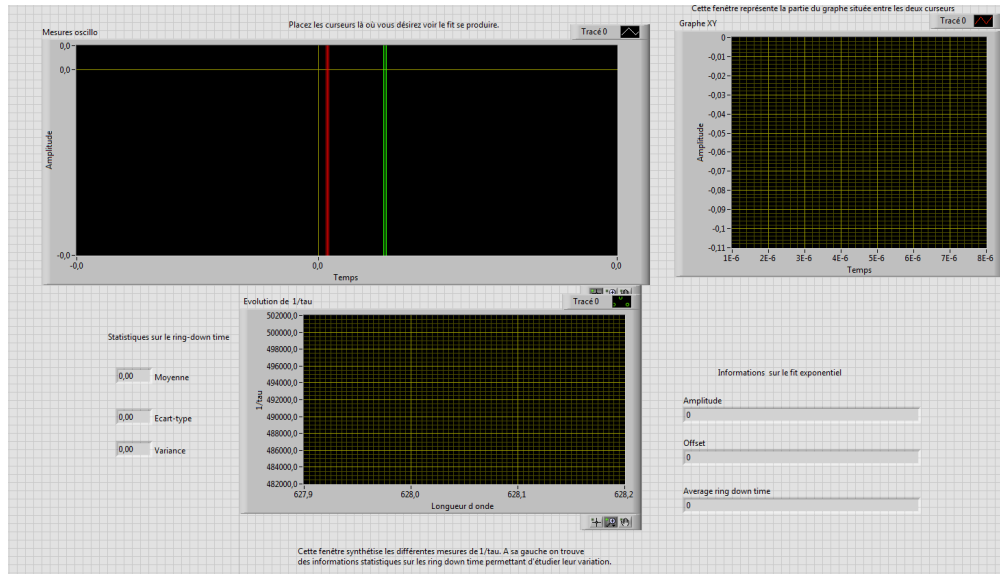


Figure B.2: Lower part of the front panel

This front panel has been designed to be as user friendly as possible. On the upper part (Figure B.1), the parameters of the oscilloscope can be adapted before performing the measure. The channel to which the detector is connected can be changed as well as the operation mode of the oscilloscope. The averaging mode can be chosen in the drop-down menu *Acquisition type*. In the box *Average count* the number of signals to take into account for the average has to be entered (it has to be a power of 2 otherwise it can not be handled by the oscilloscope). The trigger has to be adjusted in the drop-down menus *Trigger source*, *Trigger level* and *Edge slope* respectively for the channel to which the trigger is designed, the trigger level and the type of slope that triggers the trigger.

The window below will show the raw signal obtained by the oscilloscope after the application of the average. To the left of this window, the wavelength range have to be adjusted before launching the routine.

The window at the left of the lower part of the front panel (Figure B.2) is the one that allows to place the cursors between the values where the exponential fit has to be done. The position of these cursors will be displayed to the right of the window of the upper part of the front panel. The window at the right of the lower part will represent the signal between the two cursors, it will be a check to be sure that the fit is performed on a convenient set of data. The window of the lower part of the front panel represents the evolution of the inverse of the ring-down time as a function of the wavelength (the one computed by the routine). This evolution will be displayed at the end of the measurement. On the left of this figure, some statistical information about the inverse of the ring-down time are provided whereas on the right of this figure real-time information on the fit are provided.

B.2 Back panel

Figures B.3, B.4, B.5 and B.6 represent the different parts of the back panel of the LABVIEW routine that has been designed.

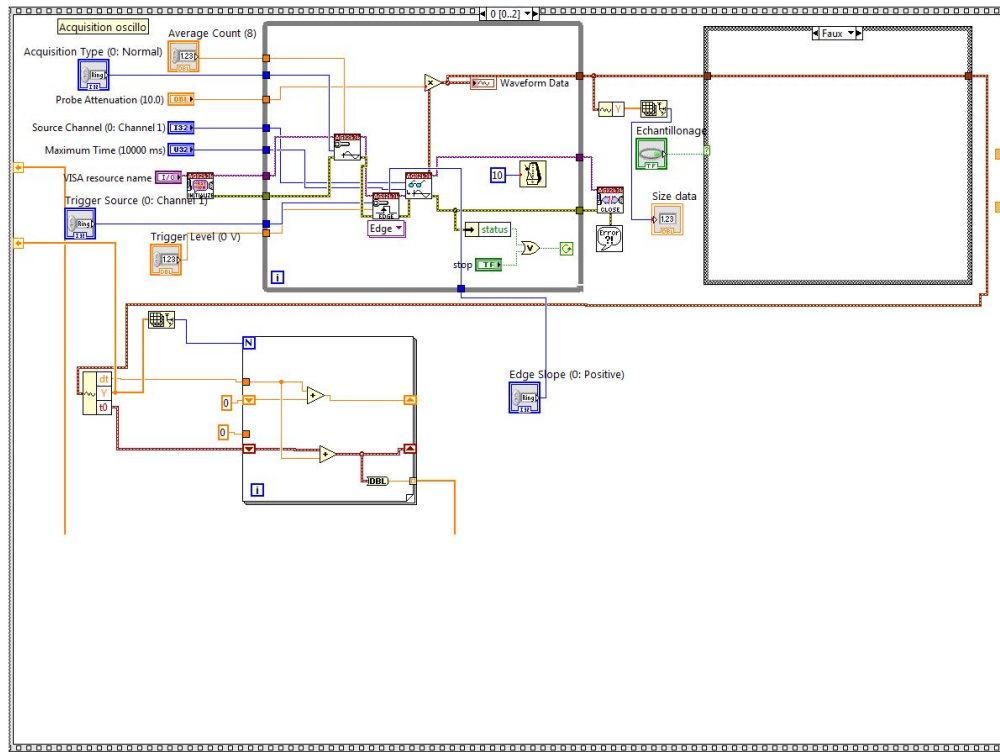


Figure B.3: Part of the routine that handles the data acquisition

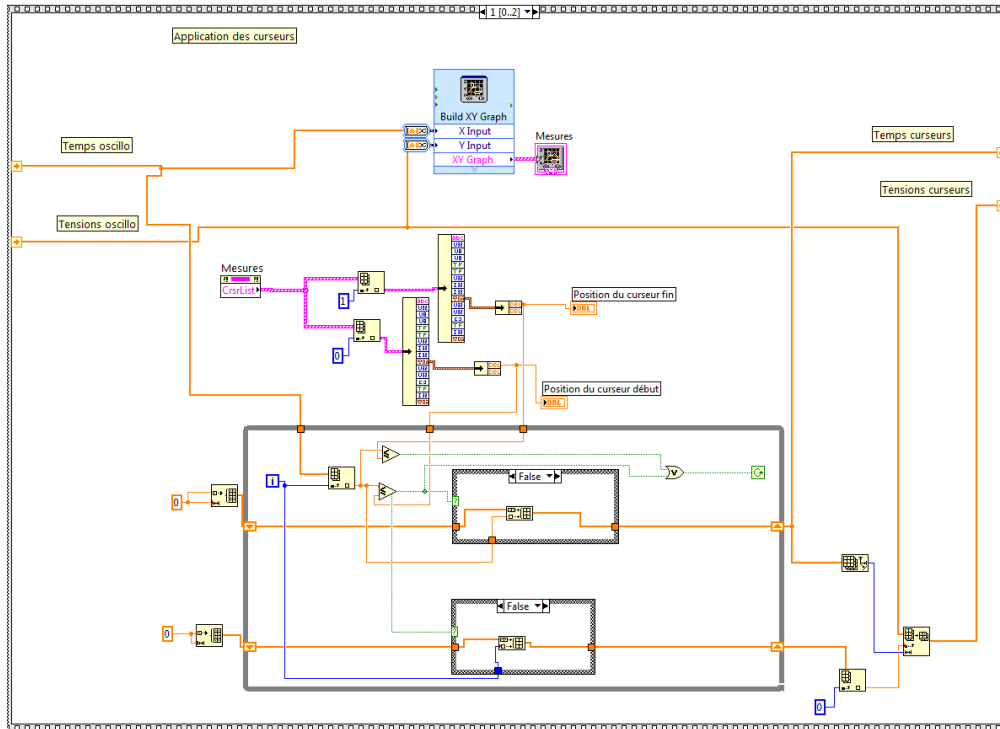


Figure B.4: Part of the routine that handles the cursors and the selection of the subwindow in which the fit will be performed afterwards.

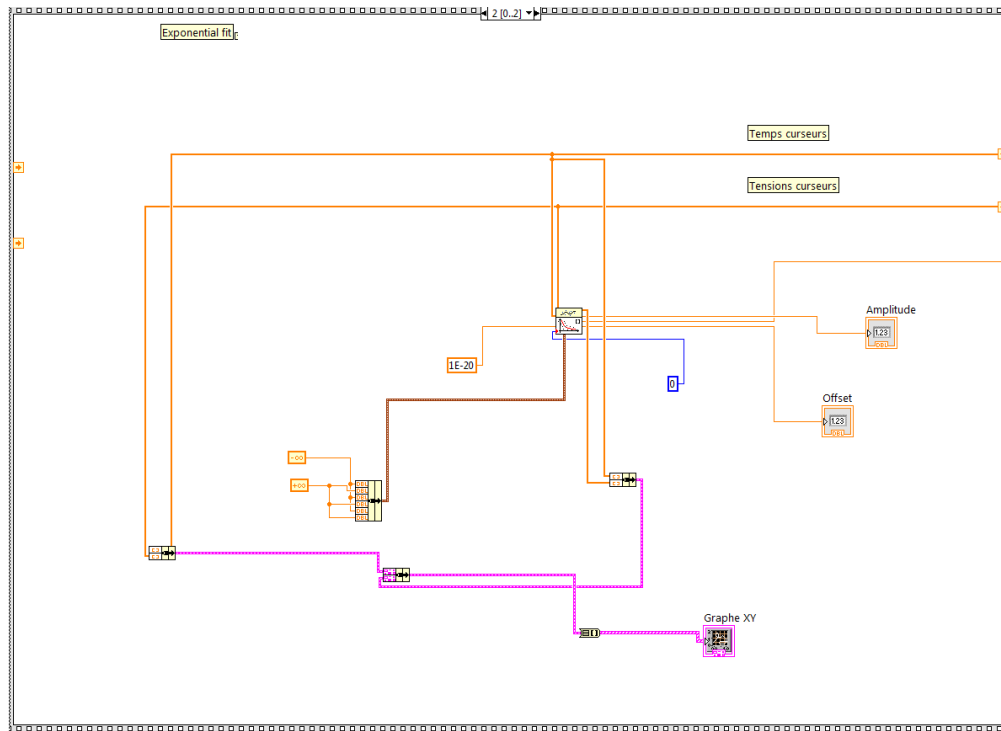


Figure B.5: Part of the routine that achieves the exponential fit of the data

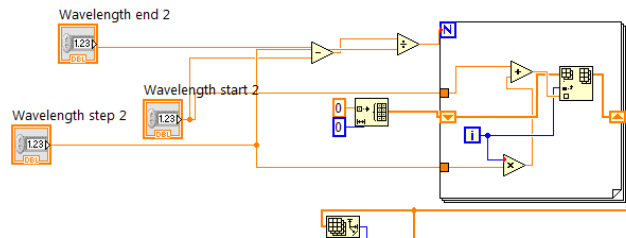


Figure B.6: Part of the routine that builds the wavelength vector

Figures B.3, B.4 and B.5 represent three successive components of an event structure. The first one is about the data acquisition and the adjustment of the oscilloscope. This first part is built to work with a given type of oscilloscope but it can be extended to other oscilloscope by replacing the VI related to the oscilloscope by the ones of the oscilloscope effectively used. This first part also creates the time and tension vectors that will be used afterwards to achieve the exponential fit of the data.

The second step of the event structure is the one that handles the cursors. The positions of the cursors are read and the tension and time vectors are adapted to this new window. This second part also provides information about the cursors by displaying their position and representing the signal in the window that they defined.

The third sequence of the event structure is the one that performs the exponential fit of the data. This is done thanks to a built-in VI of LABVIEW that requires as parameters the range in which the fitted parameters must be considered and the method that has to be used. It could be

possible to replace this VI by a function especially designed for the measurement of ring-down time that could be faster than the built-in one[31].

Figure B.6 represents the part of the routine that creates the wavelength vector considered during the measurement.

Source code

This appendix gathers all the source codes that have been used for the simulation performed in the frame of this master thesis. The different codes are presented and briefly explained.

C.1 Mode matching calculations

This is the function that computes the position of the lenses in order to proceed to mode matching.

```

1 function [evaluation,Distances] = resolution(f1, f2, lambda,xi, qfinal)
2 %Antoine De Comite – version 2.1
3 %Resolution This function compute the optimal position of lenses for
  mode
4 %matching
5 % This function will compute the optimal position of two convex
  lenses
6 % in order to proceed to mode matching. The system has been obtained
  for
7 % propagation in air.
8 % The different iterates of the method will be given in the command
9 % window as well as the final value of the distances d1, d2 and d3.
10 % Inputs : -f1 is the focal length of the first lens [m]
11 %           -f2 is the focal length of the second lens [m]
12 %           -lambda is the wavelength of the beam [m]
13 %           -xi is an initial iterate to proceed to minimisation
14 %           -qfinal is the beam parameter at the left side of the cavity
15 % Outputs : -evaluation gives the q-parameter at the left side of the
16 %            cavity for the distances obtained after resolution
17 %            -distances is a vector containing the three distances
18
19
20 % 1) Computation of the q-parameters of the laser and the cavity
21 w0=2e-3;% Waist of the laser [m]
22 qinit=(-1i*lambda/(pi*w0^2))^(-1);
23
24 te=6.35e-3;%Thickness of the output mirror [m]
25 n=1.4570;%Refractive index of the medium in the output mirror

```

```

26 Aout=[1 0; 0 n]*[1 te; 0 1]*[1 0; (1-n)/(600e-3*n) 1/n];%ABCD matrix of
    the output mirror
27 qlleft=(Aout(1,1)*qfinal + Aout(1,2))/(Aout(2,1)*qfinal + Aout(2,2));
28
29
30
31 % 2) System of equations
32 function System=equatbis(x)
33     % Introduction of the intermediate matrix
34     A1=1 - x(3)/f1 + (x(3)*x(2))/(f1*f2) - x(2)/f2 - x(2)/f1;
35     A2=x(1) + x(3) - (x(1)*x(3))/f1 + x(2) - (x(2)*x(1))/f1 + (x(1)
        *x(3)*x(2))/(f1*f2) - x(2)/f2*(x(1)+x(3));
36     A3=x(3)/(f1*f2) - 1/f2 - 1/f1;
37     A4=1 - x(1)/f1 + (x(1)*x(3))/(f1*f2) - x(1)/f2 - x(3)/f2;
38     qi=(A1*qinit+A2)/(A3*qinit+A4);
39     System(1)=real(qi)-real(qlleft);
40     System(2)=abs(imag(qi))-abs(imag(qlleft));
41 end
42
43 % 3) Resolution of the system using fsolve. The parameter TolFun has
    been
44 % changed because of the small value of the q-parameter in order to
    proceed
45 % to a more accurate resolution.
46
47 myfun = @equatbis;
48 options = optimoptions('fsolve','Display','iter','MaxFunEvals',1000,'
    TolFun', 1e-10,'Algorithm','levenberg-marquardt');
49 [Distances,fval] = fsolve(myfun,xi,options)%This line will print the
    final value of the minimisation
50
51
52
53 % 4) Evaluation of the q-parameter at the end of the minimisation
    procedure
54 function qeval=Evalq(X,qinit)
55     A1=1 - X(3)/f1 + (X(3)*X(2))/(f1*f2) - X(2)/f2 - X(2)/f1;
56     A2=X(1) + X(3) - (X(1)*X(3))/f1 + X(2) - (X(2)*X(1))/f1 + (X(1)
        *X(3)*X(2))/(f1*f2) - X(2)/f2*(X(1)+X(3));
57     A3=X(3)/(f1*f2) - 1/f2 - 1/f1;
58     A4=1 - X(1)/f1 + (X(1)*X(3))/(f1*f2) - X(1)/f2 - X(3)/f2;
59     qeval=(A1*qinit+A2)/(A3*qinit+A4);
60 end
61 evaluation=Evalq(Distances,qinit);
62
63
64 end

```

C.2 Temperature calculations

This code is the one that performs the computation of the temperature profile in the cryogenic cell.

```

1 function [ T ] = StatResolution( nx, Text, H, K )
2 format long;
3 %STATRESOLUTION is a function that computes the temperature profile
   inside a cylindrical cryogenic cell
4 % Inputs : nx is the discretisation step, the meshgrid is composed of
   squares
5 %          rho is the density of the considered gas [kg/m^3]
6 %          Text is the external temperature [K]
7 %          C is the heat capacity of the gas [J/(kg/K)]
8 %          h is the convection coefficient of the ambient gas [W/(mK)]
9 %          k is the coefficient of heat conduction of the gas in the
   cell [W/(m^2K)]
10 %
11 % Outputs : T is a matrix containing the temperature at any point for
   the final iterate
12 %
13 % This function computes the temperature profile inside the cell for
   the
14 % problem explains in this written dissertation. This code involves
   both
15 % the application of the boundary conditions and the resolution of the
16 % heat transfer equation.
17 % Antoine De Comite
18
19 %% Parameters of the problem
20
21 L=140; %Length of the cell
22 W=1.4; %Width of the cell
23 dx=L/nx; %Handling of the meshgrid
24 dy=dx;
25 T=300*ones(nx/100,nx); %Application of the initial iterate (all the
   points are at 300K)
26
27 %% Applications of the boundary conditions
28 T(1,:)=77; T(end,:)=77; %Dirichlet conditions on the upper and lower
   sides
29 %Robin conditions
30 Tlim=polyval(polyfit([0 0.7 1.4],[77 ((H-K)/(K+H)*Text) 77],2),
   linspace(0,1.4,nx/100));
31 for i=2:nx/100-1
32     T(i,end)=Tlim(i);
33     T(i,1)=Tlim(i);
34 end
35
36 niter=20000; %Determination of the number of iterations

```

```

37 %Computation of the temperature based on the formula given in the
    dissertation
38 while(niter~=0)
39     for i=2:nx/100-1
40         for j=2:nx-1
41             T(i,j)=1/(2/(dx^2)+2/(dy^2)) * ((T(i-1,j)+T(i+1,j))/(dy^2)
                + (T(i,j-1)+T(i,j+1))/(dx^2));
42         end
43     end
44     niter=niter-1;
45 end
46
47 %%Handling of the plot
48 X=linspace(0,L,nx);
49 Y=linspace(0,W,nx/100);
50 figure;
51 hold on;
52 surf(X,Y,T,'EdgeColor','none')
53 xlabel('x')
54 ylabel('y')
55 zlabel('z')
56 end

```

C.3 Computation of the energy levels

This code is the code that computes the energy levels of the water molecule in its fundamental vibrational state.

```

1 function [ H, Energies, Jvector, V] = WaterHamiltonian( Jmax, Be)
2 %WaterHamiltonian This function computes the rotational hamiltonian of
    the
3 %water molecule and find its proper energies thanks to diagonalisation.
4 % Inputs: -Be is the equilibrium value of the rotational constant
    along the b-axis
5 %         -Jmax is the maximal angular momentum considered in the
    problem
6 %
7 % Outputs: -H is the hamiltonian matrix that has been computed
8 %          -Energies are the eigenenergies of the hamiltonian
9 %          -Jvector is a vector containing the value of the J quantum
    number for the different energy levels
10 %          -V contains the terms of the linear combination that
    express this wave function in terms of the
11 %          ones of the wave functions basis set
12 %
13 % Antoine De Comite
14
15 %%Set of rotational constants
16 Ae = 27.88063094; Ce = 9.277708381;

```

```

17 DeltaJ = 1.254008198e-3; DeltaJK = -5.767750168e-3; DeltaK =
    0.03246545982;
18 deltaJ = 5.073643981e-4; deltaK = 1.369287282e-3;
19 HJ = 5.222146049e-7; HJK = -1.403671069e-6; HKJ = -1.6995375e-5; HK =
    1.245204107e-4;
20
21
22 H=BuildBlock(0, Ae, Be, Ce);
23 for j = 1:Jmax
24     H = [H zeros(length(H(1,:)), 2*j+1); zeros(2*j+1, length(H(1,:)))
          BuildBlock(j, Ae, Be, Ce)];
25 end
26
27
28 function [block] = BuildBlock(J, Ae, Be, Ce)
29     %BUILDBLOCK is a function designed to compute the value of the
30     %block elements of the Hamiltonian matrix.
31     % Inputs : J is the considered angular momentum
32     %          Ae, Be and Ce are the rotation constants of the
33     %          concerned molecule
34     %
35     % Outputs : block is a block matrix (2*J+1) containing the
36     %            block
37     % element of the hamiltonian.
38     block = zeros(2*J+1);
39     kmap = -J:J;
40     multJ = (Be+Ce)/2;
41     multJz = (Ae - (Be+Ce)/2);
42     multJplus = (Be-Ce)/4;
43     multJminus = (Be-Ce)/4;
44     if J==0
45         block = multJ*J*(J+1)+multJz*kmap^2;
46     else
47         for i = 1:2*J+1
48             if (i<3 && i>(2*J-1))
49                 block(i,i) = multJ*J*(J+1)+multJz*kmap(i)^2-DeltaJ*
                    J^2*(J+1)^2-DeltaJK*J*(J+1)*kmap(i)^2-DeltaK*
                    kmap(i)^4+HJ*J^3*(J+1)^3+HJK*J^2*(J+1)^2*kmap(i)
                    ^2+HKJ*J*(J+1)*kmap(i)^4*HK*kmap(i)^6;
50             elseif (i<3 && i<=(2*J-1))
51                 block(i, [i, i+2]) = [multJ*J*(J+1)+multJz*kmap(i)
                    ^2-DeltaJ*J^2*(J+1)^2-DeltaJK*J*(J+1)*kmap(i)^2-
                    DeltaK*kmap(i)^4+HJ*J^3*(J+1)^3+HJK*J^2*(J+1)^2*
                    kmap(i)^2+HKJ*J*(J+1)*kmap(i)^4*HK*kmap(i)^6, (
                    multJminus-deltaJ*J*(J+1)-0.5*deltaK*(kmap(i+2)
                    ^2+kmap(i)^2)+HJ*J^2*(J+1)^2+0.5*HK*(kmap(i+2)
                    ^4+kmap(i)^4)+0.5*HJK*J*(J+1)*(kmap(i+2)^2+kmap(
                    i)^2))*sqrt((J*(J+1)-kmap(i+1)*kmap(i+2)))*(J*(J
                    +1)-kmap(i)*kmap(i+1)))]];

```

```

51         elseif (i>=3 && i>(2*J-1))
52             block(i,[i-2, i]) = [(multJplus-deltaJ*J*(J+1)-0.5*
                                   deltaK*(kmap(i-2)^2+kmap(i)^2)+HJ*J^2*(J+1)
                                   ^2+0.5*HK*(kmap(i-2)^4+kmap(i)^4)+0.5*HJK*J*(J
                                   +1)*(kmap(i-2)^2+kmap(i)^2))*sqrt((J*(J+1) -
                                   kmap(i-1)*kmap(i-2)) * (J*(J+1) - kmap(i)*kmap(i
                                   -1))), multJ*J*(J+1)+multJz*kmap(i)^2-DeltaJ*J
                                   ^2*(J+1)^2-DeltaJK*J*(J+1)*kmap(i)^2-DeltaK*kmap
                                   (i)^4+HJ*J^3*(J+1)^3+HJK*J^2*(J+1)^2*kmap(i)^2+
                                   HKJ*J*(J+1)*kmap(i)^4*HK*kmap(i)^6];
53         else
54             block(i,[i-2, i ,i+2]) = [(multJplus-deltaJ*J*(J+1)
                                   -0.5*deltaK*(kmap(i-2)^2+kmap(i)^2)+HJ*J^2*(J+1)
                                   ^2+0.5*HK*(kmap(i-2)^4+kmap(i)^4)+0.5*HJK*J*(J
                                   +1)*(kmap(i-2)^2+kmap(i)^2))*sqrt((J*(J+1) -
                                   kmap(i-1)*kmap(i-2)) * (J*(J+1) - kmap(i)*kmap(i
                                   -1))), multJ*J*(J+1)+multJz*kmap(i)^2-DeltaJ*J
                                   ^2*(J+1)^2-DeltaJK*J*(J+1)*kmap(i)^2-DeltaK*kmap
                                   (i)^4+HJ*J^3*(J+1)^3+HJK*J^2*(J+1)^2*kmap(i)^2+
                                   HKJ*J*(J+1)*kmap(i)^4*HK*kmap(i)^6, (multJminus-
                                   deltaJ*J*(J+1)-0.5*deltaK*(kmap(i+2)^2+kmap(i)
                                   ^2)+HJ*J^2*(J+1)^2+0.5*HK*(kmap(i+2)^4+kmap(i)
                                   ^4)+0.5*HJK*J*(J+1)*(kmap(i+2)^2+kmap(i)^2))*
                                   sqrt((J*(J+1) - kmap(i+1)*kmap(i+2)) * (J*(J+1)
                                   - kmap(i)*kmap(i+1)))];
55         end
56     end
57 end
58 end
59
60 end
61 [V, Lambda] = eig(H); % Computation of the eigenenergies of the
62 hamiltonian
63 Jvector = zeros(length(H(1,:)),1);
64 Energies = diag(Lambda) ;
65
66
67 for i=2:length(Jvector)
68     Jvector(i)=floor(sqrt(find(V(:,i)~=0,1)));
69 end
70 end

```

C.4 Simulation of the spectrum

This code is the one used to simulate the spectrum of the water molecule. It applies the selection rules and computes an approximation of the intensity of the transitions.

```

1 % Simulation of the spectrum of the water molecule based on
   rovibrational
2 % levels of the molecule. This part of the script only presents the
   implementation
3 % of the selection rules as well as the computation of the intensity.
4 %
5 % Antoine De Comité
6
7
8 %% Conditionning of the execution
9 close all; clc; clear all;
10 format long;
11
12
13
14 %% Constants
15 Na = 6.033e32;% Avogadro's constant
16 kb=1.38e-23;% Boltzmann's constant
17 kbcm=0.6950805942;% Boltzmann's constant in [cm-1]
18 T=300;% Temperature
19 h=6.62e-34;% Planck's constant
20 c=3e8;%Speed of light
21 p=1.01325;% Atmospheric pressure
22 Lambda=0;% Molecular quantum number representing the projection of J
   on the intermolecular axis
23
24 %%% Effective proceeding %%%
25 %% 1. Importation and handle of the file containing the different
   energy levels.
26
27 DataFile = xlsread('mmc2.xlsx', 'A1:I18486');
28
29 % Acquisition of the vibrational constants
30 nu1 = DataFile(:,1);
31 nu2 = DataFile(:,2);
32 nu3 = DataFile(:,3);
33
34 % Acquisition of the rotational constants
35 J = DataFile(:,4);
36 Ka = DataFile(:,5);
37 Kc = DataFile(:,6);
38
39 % Acquisition of the energies of the eigenstates
40
41 E = DataFile(:,7);
42 inten = DataFile(:,9);
43
44
45

```

```

46
47
48
49 %%
50 %%2. Selection of the low energy levels (considered as ground states).
51
52 Indexes1 = find(J<=6 & nu1==0 & nu2==0 & nu3==0); % This vector
    contains the indexes of the ground states
53 % The informations over the ground states will be compiled in a matrix.
    Each row of this matrix contains a ground state whereas each column
54 % contains a specific information about the considered state.
55 GroundStates = [nu1(Indexes1), nu2(Indexes1), nu3(Indexes1), J(Indexes1
    ), Ka(Indexes1), Kc(Indexes1), E(Indexes1), inten(Indexes1)];
56 % Study of the population factor
57 PopBase = (2*mod(GroundStates(:,5)+GroundStates(:,5),2)+1) .* exp(-
    GroundStates(:,7)/(kbcm*298));
58
59
60
61
62
63 %% 3. Selection of the excited states that will be probed by the laser
    (620 —> 680 nm). The selection rules are used to store the
    authorized transition.
64 %% These transitions are stored into a .txt file named Spec.txt.
65
66 lbound = 15000; % Lower bound on the wavenumber
67 ubound = 16000; % Upper bound on the wavenumber
68
69 Indexes2 = find(E>lbound & E<ubound); % This vector contains the
    indexes of the excited states probed by the laser. They will also be
    stored into
70 % matrix.
71 ExcitedStates = [nu1(Indexes2), nu2(Indexes2), nu3(Indexes2), J(
    Indexes2), Ka(Indexes2), Kc(Indexes2), E(Indexes2), inten(Indexes2)
    ];
72
73
74 %% 3. Application of the selection rules (complicated part...)
75 % For each ground state, one will compute the possible transitions (
    characterised by selection rules)
76
77 EnergiesTransitions = zeros(0,0); % This vector contains the different
    energies corresponding to the allowed transitions
78 Jtrans = zeros(0,0);
79 ExpoVec = zeros(0,0);
80 ExpoVecBis = zeros(0,0);
81 for i=1:length(Indexes1)
82     AllowedIndexes = find((mod(ExcitedStates(:,3),2)==0 & (abs(

```

```

ExcitedStates(:,4)-GroundStates(i,4))<=1) & (mod(abs(
ExcitedStates(:,5)-GroundStates(i,5)),2)==1) & (mod(abs(
ExcitedStates(:,6)-GroundStates(i,6)),2)==1) & (2*ExcitedStates
(:,1)+ExcitedStates(:,2)+2*ExcitedStates(:,3))~=0) | (mod(
ExcitedStates(:,3),2)==1 & (abs(ExcitedStates(:,4)-GroundStates(
i,4))<=1) & (mod(abs(ExcitedStates(:,5)-GroundStates(i,5)),2)
==0) & (mod(abs(ExcitedStates(:,6)-GroundStates(i,6)),2)==1) &
(2*ExcitedStates(:,1)+ExcitedStates(:,2)+2*ExcitedStates(:,3))
~=0));
83 Jtrans = [Jtrans [ExcitedStates(AllowedIndexes,4) GroundStates(i,4)
*ones(size(ExcitedStates(AllowedIndexes,4))) ExcitedStates(
AllowedIndexes,1) ExcitedStates(AllowedIndexes,2) ExcitedStates(
AllowedIndexes,3) ExcitedStates(AllowedIndexes,5) ExcitedStates(
AllowedIndexes,6) 2*ExcitedStates(AllowedIndexes,1)+
ExcitedStates(AllowedIndexes,2)+2*ExcitedStates(AllowedIndexes
,3) GroundStates(i,4)*ones(size(ExcitedStates(AllowedIndexes,1))
) GroundStates(i,5)*ones(size(ExcitedStates(AllowedIndexes,1))
) GroundStates(i,6)*ones(size(ExcitedStates(AllowedIndexes,1))
) GroundStates(i,1)*ones(size(ExcitedStates(AllowedIndexes,1))
) GroundStates(i,2)*ones(size(ExcitedStates(AllowedIndexes,1))
) GroundStates(i,3)*ones(size(ExcitedStates(AllowedIndexes,1))
) '];
84 EnergiesTransitions = [EnergiesTransitions [(ExcitedStates(
AllowedIndexes,7)-GroundStates(i,7)) GroundStates(i,7)*ones(
length(AllowedIndexes),1) '];
85 ExpoVec = [ExpoVec [(1+2*mod(ExcitedStates(AllowedIndexes,5)+
ExcitedStates(AllowedIndexes,6),2)).*(2*GroundStates(i,4)*ones(
size(ExcitedStates(AllowedIndexes,4)))+1).*exp(-GroundStates(i
,7)*ones(length(AllowedIndexes),1)/(kbcm*298))] '];
86 ExpoVecBis = [ExpoVecBis [(1+2*mod(ExcitedStates(AllowedIndexes,5)+
ExcitedStates(AllowedIndexes,6),2)).*exp(-GroundStates(i,7)*ones
(length(AllowedIndexes),1)/(kbcm*298))] '];
87
88 end

```

User guide of the dye laser

This appendix presents the steps that have to be followed in order to start up the dye laser.

Switching the laser on

1. Switch on the switch on the wall.
2. Initiate the water circulation in the laser and in the dyes of the laser (the two lower valves). The one on the right has to be fully open whereas only a quarter of turn is enough for the second one.
3. Plug the dye and launch its circulation.
4. Switch on the switches off the grey box (from the bottom to the top).
5. Turn the key and wait for the count down to finish (more or less 15 seconds)
6. On the control pad, push on *charge* and *fire* 4-5 times. All the lights have to be switched on.
7. On the control pad, push on *auto manual*. Flash only will be printed on the screen.
8. Push on *start*.
9. Wait about 5 minutes, the needle that measures the temperature of the Nd:YAG laser has to be at the level of the green line on the dial at the bottom of the grey box.
10. Push on *stop*.
11. On the control pad, launch the *PRGM3* by pushing on *PRGM* (printed on the screen).
12. Push on *activate*.
13. Push on *shutter*.
14. Push on *Q-switch* twice.
15. Push on *start*.

Switching the laser off

1. Push on the *Stop* knob on the control pad.
2. Turn the key
3. Switch off the switches from top to bottom.
4. Unplug the dye
5. Wait 5 minutes before stopping the water circulation.

