

École polytechnique de Louvain

Design, characterization and validation of a Ku-band chirped-pulse Fourier transform microwave spectrometer

Author: **Simon COLLIGNON**

Supervisors: **Clément LAUZIN, Dimitri LEDERER**

Readers: **Matthieu GÉNÉVRIEZ, Isabelle HUYNEN**

Academic year 2021–2022

Master [120] in Electrical Engineering

Abstract

With its outstanding ability at probing a frequency range larger than 10 GHz in one acquisition, the chirped-pulse Fourier transform spectrometer has revolutionized the field of gas phase microwave spectroscopy. The pure rotational spectra collected by this instrument display a high-resolution and reach high-sensitivity levels by virtue of the phase-reproducible chirped-pulse measurements. With the ever-growing advances in digital electronics, it is now manageable to perform the chirp generation with a direct digital synthesizer and the detection of the molecular emission with a digitizer card or a USB oscilloscope. In this work, a spectrometer that includes both of those features is presented. The instrument aims to explore the Ku-band of the microwave range, where the molecular sample is investigated either in a waveguide static cell or in a supersonic jet expansion. To this end, the instrument is characterized and optimized with the development of a fast averaging scheme and a post-processing pipeline. For the supersonic jet expansion experiment, we present a novel approach to optimize the sensitivity of the instrument by polarizing the molecular beam through a slotted waveguide.

Acknowledgement

I wish to acknowledge the help of several persons without whom this thesis would not have been possible.

First of all, I would like to express my sincere gratitude to my supervisors Prof. Clément Lauzin and Prof. Dimitri Lederer for their guidance and availability throughout the academic year.

Furthermore, I am particularly grateful to Dr. Brian Hays for his patience and support as he taught me most of the experimental and post-processing techniques.

Then, I would like to thank Marc Daman and Guilhem Vanlancker for their constant assistance to maintain the instrument, and for the instructive discussions.

In addition, I also would like to thank Thomas Corbro for his technical drawings and for the fabrication of the waveguide prototypes.

I also wish to thank Prof. Matthieu Génévriez and Prof. Isabelle Huynen for the reading and the assessment of this thesis.

Contents

1	Introduction	1
2	State of the art	3
2.1	Theory	3
2.1.1	Formulation of light-matter interactions	4
2.1.2	Macroscopic polarization	6
2.1.3	Constant frequency pulses	8
2.1.4	Chirped-pulses and linear fast passage	11
2.2	Development of the CP-FTMW technique	14
2.2.1	Background	14
2.2.2	First design of the CP-FTMW spectrometer	14
2.2.3	Evolution of the CP-FTMW spectrometer	17
3	Design and characterization of the CP-FTMW spectrometer	19
3.1	Excitation module	19
3.1.1	Direct Digital Synthesis	19
3.1.2	Upconversion	24
3.1.3	Amplification	25
3.2	Waveguide static cell	26
3.3	Detection module	28
3.4	Timing & synchronisation	29
3.5	RF chains analysis	30
4	First results and improvements of the CP-FTMW spectrometer	33
4.1	First spectra	33
4.2	Digitizer & Data acquisition	36
4.3	Post-processing	39
4.3.1	Infinite impulse response filtering	39

4.3.2	Pattern filtering	41
4.3.3	Background subtraction	44
5	Slotted waveguide in supersonic jet expansion	48
5.1	Theoretical considerations	49
5.2	Electromagnetic simulations of the slotted waveguide	50
5.2.1	Design parameters and constraints	50
5.2.2	Design specifications	52
5.2.3	Design motivations	52
5.2.4	Simulation results	54
5.3	Results	58
5.3.1	S-parameters measurements	58
5.3.2	Spectra	60
5.3.3	Discussion	62
6	Conclusion and perspectives	63

Chapter 1

Introduction

Invented in the mid-2000s, the first chirped-pulse Fourier transform microwave (CP-FTMW) spectrometer allows for the detection of broadband molecular rotational spectra over a 10 GHz bandwidth in one shot, where previous microwave spectrometer designs were limited to ~ 1 MHz bandwidth per acquisition. [1, 2] Furthermore, the spectra collected by the CP-FMTW instrument display a high-resolution and reach decent sensitivity levels over short measurement times compared to the previous designs. This spectrometer is therefore an ideal tool to quickly determine the chemical composition of molecular sample based on the acquired survey spectrum. In these experiments, the spectrometer produces a broadband microwave (MW) pulse which excites the molecular gas over a large frequency range. In reaction to this excitation, the molecules emit an electromagnetic response, referred to as the free induction decay (FID), which is detected by a high-speed oscilloscope. The molecular spectrum is finally obtained upon the Fourier transformation (FT) of the detected time-domain FID.

With the ever-growing advances in digital electronics and monolithic microwave integrated circuits (MMIC), it was first demonstrated by Finneran *et al.* [3] that the bulky and expensive arbitrary waveform generator (AWG), employed in the original CP-FTMW design to generate the microwave pulse, can be replaced by a compact and affordable direct digital synthesizer (DDS). Moreover, other CP-FTMW designs have substituted the high-end oscilloscope either by a portable USB oscilloscope [4] or a digitizer card. [5] Combining these technological improvements allows for a drastic reduction in cost and footprint of the instrument, while offering a versatile CP-FTMW spectrometer design which does not compromise on its performance.

The focus of the current work is the development, characterization and validation of a low-cost, small-footprint CP-FTMW spectrometer, which operates in the Ku-band (i.e. 10-18 GHz frequency range) of the microwave spectrum. Over the course of this thesis, the following achievements have been accomplished:

1. Characterization of the spectrometer and subsequent determination of the figures of merit, namely the peak excitation power delivered by the excitation module of the instrument, the maximum electric field achievable in the waveguide static cell and the noise figure of the detection module.
2. Development of a fast averaging scheme, which improves by a factor of 35 the

data acquisition rate. Consequently, the spectrometer is capable of acquiring 10^6 FID averages in less than 9 minutes compared to the 5h25 required from the original design of this instrument.

3. Development of a custom post-processing pipeline, which removes most artefacts present in the spectra.
4. Design of a slotted waveguide with a low insertion loss over the 14-18 GHz bandwidth.

The present work is structured as follows:

In chapter 2, the state-of-the-art of the CP-FTMW technique is presented. First, the theory needed to describe the interaction between a coherent microwave radiation and a gas of two-level molecules is established. Based on this formalism, the emergence of the macroscopic polarization that occurs within the molecular gas, induced either by a constant frequency pulse or a chirped-pulse. Second, the historical development of the CP-FTMW technique is presented along with the well established cavity-FTMW technique. Finally, the main contributions of the CP-FTMW instrument to the field of microwave spectroscopy are stated.

In chapter 3, the design and the characterization of the first UCLouvain CP-FTMW spectrometer is described. To this end, the spectrometer is separated in three modules which are studied individually, with the excitation module which produces the excitation chirped-pulse, the waveguide static cell inside which the microwave-molecule interaction occurs and the detection module which detects and digitizes the subsequent molecular signal. A description of the timing sequence required to perform CP-FTMW experiments is also provided, along with the RF chain analysis of the overall instrument.

In chapter 4, a review of all the various improvements that we have gathered throughout the semester are presented in a chronological order to portray the iterative nature of the spectrometer development. We focus to a great extent on the data acquisition and the data post-processing since a large part of our progress were achieved in these areas.

In chapter 5, the instrument is moved from the waveguide static cell to the FANTASIO supersonic jet expansion setup. Then, a novel approach to polarize the molecular sample in supersonic jet conditions by the means of a slotted waveguide is developed, based on the cartography of the supersonic jet and the electromagnetic simulations conducted with the CST software. [6] Finally, the performances of the slotted waveguide are assessed with first, the S-parameters VNA measurements and second, the actual spectra collected during jet-pulsed CP-FTMW experiments.

Chapter 2

State of the art

In this chapter, we present the state of the art of the chirped-pulse Fourier transform microwave (CP-FTMW) technique, which has been proven to be a transformative tool in the realm of molecular rotational spectroscopy. To better understand the needs for such instruments and their design, we first identify the main physical concepts involved in the light-matter interactions, which not only provide insights about the underlying mechanisms of microwave spectroscopy but will also serve as useful figures of merit required to benchmark the spectrometer presented in the coming chapters. The second part of this chapter is dedicated to development of the CP-FTMW technique.

2.1 Theory

Molecular rotational spectrometers operate in the microwave region of the electromagnetic spectrum from 0.3 GHz to 3000 GHz, as shown in Table 2.1. Those instruments emit a coherent microwave light through the molecular gas such that the incident electromagnetic (EM) radiation interacts with the gas and induces transitions between rotational states of the molecules. Then, the molecular radiative transitions of the molecular system are detected by the spectrometer over a given frequency range, the result of such measurement is called a spectrum. Large molecules and molecular complexes tend to experience rotational transitions at the centimeter scale of the microwave wavelengths while rotational transitions of lighter molecules lie in the (sub-)mm wavelength range [7].

Table 2.1: Microwave and adjacent regions of the electromagnetic spectrum [7, 8].

	λ [cm]	$\tilde{\nu}$ [cm ⁻¹]	ν [GHz]	Type of transitions
Radio	100.0 -	0.01 -	0.3 -	Nuclear spins
cm MW	1.0 - 100.0	1.0 - 0.01	30.0 - 0.3	Rotational <i>large molecules</i>
(sub-)mm MW	0.01 - 1.0	100.0 - 1.0	3000.0 - 30.0	Rotational <i>light molecules</i>
Infrared	$7.8 \cdot 10^{-5}$ - 0.01	12800.0 - 100.0	$4.9 \cdot 10^5$ - $3 \cdot 10^3$	Vibrational

For reference, the adjacent regions of the MW range are also indicated in Table 2.1. In the radio wave region, the low photon energy (compared to MW) allows to flip within the molecules the nuclear spins in the presence of a magnetic field, which has crucial applications in the field of nuclear magnetic resonance (NMR). [8] At higher frequency, the optical segment of the electromagnetic spectrum begins with the infrared (IR) light, where the high photon energy permits to excite vibrational states of the molecules. MW photons have an insufficient energy to excite vibrational transitions and thus can only induce pure rotational transitions. For this reason, rotational spectroscopy is often equivalently referred to as microwave spectroscopy.

2.1.1 Formulation of light-matter interactions

For the sake of this theoretical formulation, the gas sample is assumed to be a collection of N two-level molecules [8, 9] where each one of them exhibits only two energy levels (as illustrated in Fig. 2.1). In this picture, N_a molecules are in the ground state $|a\rangle$ and have an energy E_a while the N_b other molecules are in the excited state $|b\rangle$ with an energy E_b , where $E_a < E_b$. The total number of molecules is thus $N = N_b + N_a$.

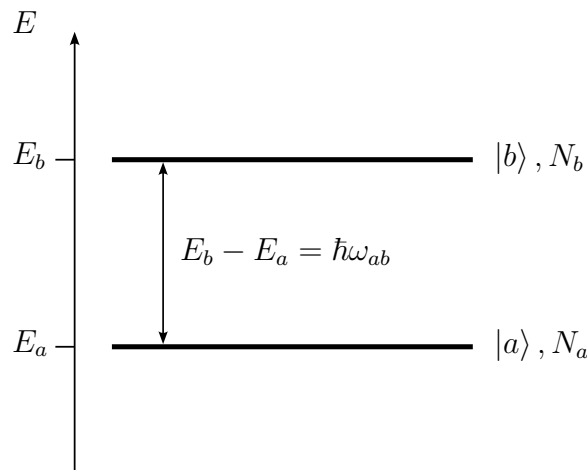


Fig. 2.1. Energy diagram of a two-level molecular system.

Then, a semi-classical treatment [10] is used to formulate the interaction between this collection of two-level quantum systems and a classical oscillating excitation electric field $\mathbf{E}^{(e)}$, which propagates along the z -axis and is linearly-polarized along the y -axis:

$$\mathbf{E}^{(e)}(\mathbf{r}, t) = E^{(e)}(\mathbf{r}, t) \cos(\omega t - kz) \hat{\mathbf{e}}_y \quad (2.1)$$

Since any molecule of the collection described above can be modelled as a unique two-level quantum system, its general wavefunction is written as:

$$|\Psi(\mathbf{r}, t)\rangle = c_a |a\rangle e^{-jE_a t/\hbar} + c_b |b\rangle e^{-jE_b t/\hbar} \quad (2.2)$$

where j is the imaginary number, while c_a and c_b are complex coefficients which describe the probability $|a|^2$ ($|b|^2$) of finding the system in the state $|a\rangle$ ($|b\rangle$) and

ensure the normalization of $|\Psi(\mathbf{r}, t)\rangle$ with $|c_a|^2 + |c_b|^2 = 1$. If the unperturbed Hamiltonian H_0 is written such that:

$$\begin{aligned} H_0 |a\rangle &= E_a |a\rangle \\ H_0 |b\rangle &= E_b |b\rangle \end{aligned} \quad (2.3)$$

Then, the perturbation induced by the oscillating electric field is taken into account by adding an interaction term $H_I(t)$ in the total Hamiltonian H of the system [11]:

$$H = H_0 + H_I(t) = H_0 + e\mathbf{r} \cdot \mathbf{E}^{(e)} \cos(\omega t) \quad (2.4)$$

where the dipole approximation is used, namely it is assumed that $kz \approx 0$ as the spatial extension a_0 of one molecule centered on z is much smaller than the wavelength $\lambda = 2\pi/k$. The interaction between the EM field and the two-level quantum system is thus fully encapsulated in the additional term $H_I(t)$ of the total Hamiltonian and the time evolution of the molecular wavefunction $|\Psi(\mathbf{r}, t)\rangle$ is given by the Schrödinger equation:

$$j\hbar \frac{\partial |\Psi(\mathbf{r}, t)\rangle}{\partial t} = (H_0 + e\mathbf{r} \cdot \mathbf{E}^{(e)} \cos(\omega t)) |\Psi(\mathbf{r}, t)\rangle \quad (2.5)$$

By applying either $\langle a|$ or $\langle b|$ on both sides of the equation above, the following system of two coupled differential equations is obtained:

$$\begin{aligned} j \frac{dc_a}{dt} &= \Omega_R \cos(\omega t) e^{-j\omega_{ab}t} c_b \\ j \frac{dc_b}{dt} &= \Omega_R \cos(\omega t) e^{-j\omega_{ab}t} c_a \end{aligned} \quad (2.6)$$

where $\omega_{ab} = (E_b - E_a)/\hbar$ and Ω_R is the Rabi frequency, defined as:

$$\Omega_R = \frac{\langle a| e\mathbf{r} \cdot \mathbf{E}^{(e)} |b\rangle}{\hbar} = \frac{E^{(e)} \langle a| ey |b\rangle}{\hbar} = -\frac{E^{(e)} \mu_{ab}}{\hbar} \quad (2.7)$$

with the transition dipole moment μ_{ab} defined as the matrix element $-\langle a| ey |b\rangle = \langle a| \mu |b\rangle$. As seen in the equations 2.6, the temporal evolution of the two-level molecule is proportional to Ω_R and thus also proportional to $E^{(e)}$ and μ_{ab} . It is already an important result as it shows that the system dynamics are not only driven by the strength of the E-field excitation, but also by the transition dipole moment μ_{ab} . In the case of pure rotational transitions, μ_{ab} is proportional to the permanent dipole moment μ_0 of the molecule [8]. Consequently, the rotational transitions of nonpolar molecules (i.e., molecules for which $\mu_0 = 0$) cannot interact with the radiation, as $\Omega_R = 0$. This is an intuitive result since classically, the net torque τ applied on a remote object by the means of an electric field is given by $\tau = \mathbf{d} \times \mathbf{E}$. Therefore, the rotational kinetic energy of the object cannot be changed by the E-field interaction if the dipole moment $\mathbf{d}$ is equal to 0.

The difference between the frequency of the incident E-field and the frequency ω_{ab} of the molecular transition $|a\rangle \rightarrow |b\rangle$ is defined as the detuning frequency and is thus $\delta = \omega - \omega_{ab}$. When δ is equal to zero, the molecular system is said to be

resonant. In this condition, the coupled equations 2.6 admit closed-form solutions. For instance, $|c_b(t)|^2$, the probability of finding the molecular system the upper state $|b\rangle$, is expressed as:

$$|c_b(t)|^2 = \frac{\Omega_R^2}{\Omega^2} \sin^2\left(\frac{\Omega t}{2}\right) \quad (2.8)$$

where $\Omega^2 = \Omega_R^2 + \delta^2$. The response of the molecular system to an incident EM field is depicted in Fig. 2.2, where the detuning frequency is set to 0 (on-resonance), $\Omega_R/2$ (near-resonance) and $1000\Omega_R$ (off-resonance). While on-resonance, the EM

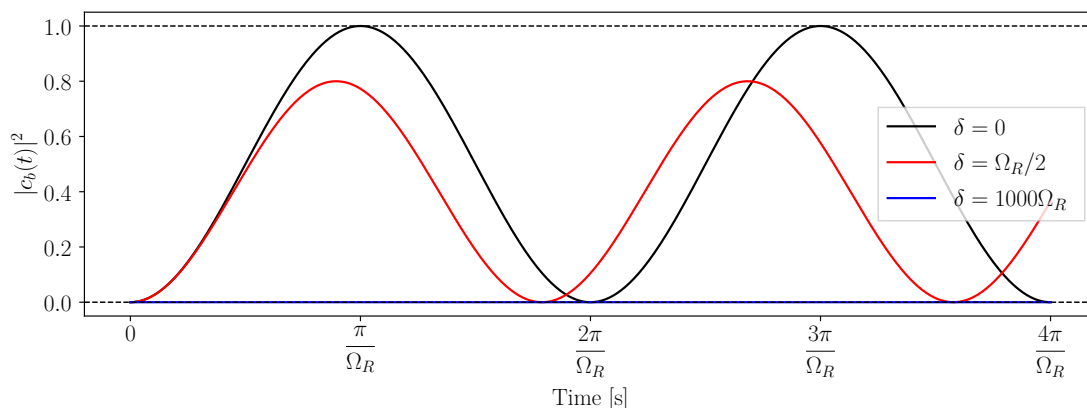


Fig. 2.2. Rabi oscillations of the two-level molecular system, with $\delta = 0, \Omega_R/2, 1000\Omega_R$.

field drives the molecular system back and forth between the ground state ($|c_b|^2 = 0$) and the excited state ($|c_b|^2 = 1$) at the Rabi frequency Ω_R , where this regime is known as Rabi oscillations (or Rabi cycling). In this regime, the molecular system starts from its ground state $|a\rangle$ at $t = 0$ and undergoes a full state swap $|a\rangle \rightarrow |b\rangle$ after a time $t = \pi/\Omega_R$. In near-resonance ($\delta = \Omega_R/2$), the system won't be able to reach $|c_b|^2 = 1$ and oscillates slightly faster than the Rabi frequency due to the contribution of δ in the driving frequency Ω . Finally, in off-resonance, the molecular system is no longer driven efficiently by the microwave light, as $\Omega \gg \Omega_R$.

2.1.2 Macroscopic polarization

In the context of the collection of N two-level molecules defined above, $|c_b(t)|^2$ is equal to N_b/N and thus describes the normalized population of molecules in the excited state $|b\rangle$. While the evolution of the populations as illustrated in Fig. 2.2 is convenient to define the quantities of interest such as Ω_R and δ involved in the light-matter interactions, the populations $|c_a(t)|^2$ and $|c_b(t)|^2$ are not directly measured in emission spectroscopy. Indeed, the detectable signal emitted by the molecules is induced by a macroscopic dipole or polarization P , which depends of the quantities $c_a c_b^*$ and $c_b c_a^*$, referred to as the coherences.

Without entering into the details of the density matrix formalism required to derive P (a detailed description is given in Ref. [10]), its expression is directly given as

[9, 7, 12]:

$$\begin{aligned} P &= \tilde{N} \mu_{ab} \left(c_a c_b^* e^{j(\omega_{ab}t - kz)} + c_b c_a^* e^{-j(\omega_{ab}t - kz)} \right) \\ &= \tilde{N} \mu_{ab} (u \cos(\omega t - kz) - v \sin(\omega t - kz)) \end{aligned} \quad (2.9)$$

where $\tilde{N}$ is the molecular density while u and v are the in-phase and quadrature normalized components of the polarization P in a frame rotating at the frequency ω of the incident radiation $\mathbf{E}^{(e)}$. In general, for emission microwave spectroscopy techniques, the spectrometer detects the transient EM response $\mathbf{E}$ broadcast by the molecular system and governed by the following wave equation [7]:

$$\left(\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \mathbf{E} = \frac{1}{c^2 \epsilon_0} \frac{\partial^2}{\partial t^2} \mathbf{P} \quad (2.10)$$

where the source term on the right-hand-side of this equation is given by the oscillating macroscopic dipole moment $\mathbf{P}$, which may be a vector quantity. In our particular example, since $\mathbf{E}^{(e)}$ is y -planed-polarized, then $\mathbf{P}$ and thus $\mathbf{E}$ are also plane-polarized along the y -axis [7].

To describe the evolution of the components u and v of the polarization P , one must solve the optical Bloch equations, expressed as:

$$\frac{du}{dt} = \delta v - \frac{1}{T_2} u \quad (2.11a)$$

$$\frac{dv}{dt} = -\delta u + \Omega_R w - \frac{1}{T_2} v \quad (2.11b)$$

$$\frac{dw}{dt} = -\Omega_R v - \frac{1}{T_1} (w - w_0) \quad (2.11c)$$

where w is the normalized population difference and is written as $w = |c_a|^2 - |c_b|^2$ and w_0 is the population difference at thermal equilibrium. With this new set of coupled equations, it is not only possible to follow the evolution of the populations through the variable w , but also to appreciate the evolution of the transient molecular response with the components u and v of the polarization dipole P . As suggested earlier, the key quantities Ω_R and δ play an important role in those rate equations. In addition to those terms, the optical Bloch equations also include phenomenological decay terms in $1/T_2$ for the polarization components, and in $1/T_1$ for the populations.

The phenomenological relaxation constants T_1 and T_2 were first introduced in the field of nuclear magnetic resonance (NMR) which uses similar Bloch equations to describe the magnetization of spin-1/2 particles [9]. In that context, T_1 is known as the spin-lattice or longitudinal relaxation time which characterizes the time required for the spins to return to their equilibrium state by releasing energy to their environment (i.e., the lattice). T_2 is the spin-spin or transverse relaxation time and provides the characteristic time over which the ensemble of spins loses its phase coherence [13].

In MW spectroscopy, very similar relaxation processes are encountered (hence the same notations), where T_1 is the characteristic time over which the population

difference w returns to its thermal equilibrium w_0 [9], and T_2 is the time constant that characterizes how the individual rotating electric dipoles go out of phase and therefore reduce the coherent macroscopic dipole P . The physical mechanisms behind T_2 can be homogeneous such as molecule-molecule interactions (e.g., pressure broadening) but also inhomogeneous due to the velocity distribution of the molecules (e.g., Doppler broadening) [8].

2.1.3 Constant frequency pulses

At this stage, all the quantities that play an important role in the optical Bloch equations have now been introduced and allows to model the transient response of an ensemble of two-level molecules interacting with a microwave light. Based on the work of [14], the equations 2.11 have been numerically solved with a Runge-Kutta numerical method of order 4 (RK4) to illustrate and discuss this molecular response.

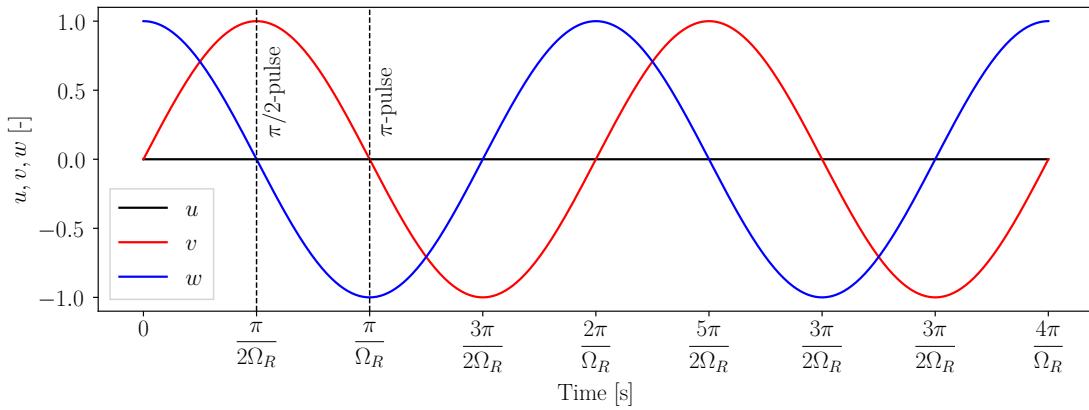


Fig. 2.3. Rabi cycling simulation with no relaxation processes (i.e. $T_1^{-1} = T_2^{-1} = 0$) and $\delta = 0$.

In Fig. 2.3, the same simulation performed previously in Fig. 2.2 is illustrated with u , v , w quantities. Just as before, the molecular system is illuminated at $t = 0$ with a resonant light (i.e., $\delta = 0$) and a given Rabi frequency Ω_R . Also, no relaxation processes are considered in this simulation. Just as before, we observe that the system undergoes a complete population swap after a time $t = \pi/\Omega_R$ (since $w = -1$), a pulse of this duration is referred to as π -pulse. More interestingly, we also see that the component v of the induced dipole moment is maximised after a pulse of duration $t = \pi/(2\Omega_R)$, which is therefore called a $\pi/2$ -pulse.

Those denominations are once again borrowed from the NMR field which makes an extensive use of such pulse sequences (e.g. Hahn spin echo [15]). In MW spectroscopy, $\pi/2$ -pulses are also very important as it guarantees to obtain the maximum macroscopic polarization and thus the maximum detectable signal emitted by the molecules.

The evolution of the normalized polarization $\tilde{P}$ is displayed in Fig. 2.4 during a $\pi/2$ -pulse sequence, where $\tilde{P}$ is simply written as:

$$\tilde{P} = u \cos(\omega t) - v \sin(\omega t) \quad (2.12)$$

For this simulation to be more realistic, a T_2 relaxation process is introduced with $T_2 = 10/\Omega_R$ (while keeping $T_1^{-1} = 0$) and a detuning frequency $\delta = \Omega_R/2$. We arbitrarily choose a Rabi frequency $\Omega_R = 2\pi \cdot 10^6$ [rad·s⁻¹] to approach a $\pi/2$ -pulse of duration $\tau_p = 0.25$ [μ s]. For the purpose of this example, the transition frequency is also arbitrarily set to $\omega_{ab} = 10\Omega_R$. At first, for $t < 0$, the molecular system rests

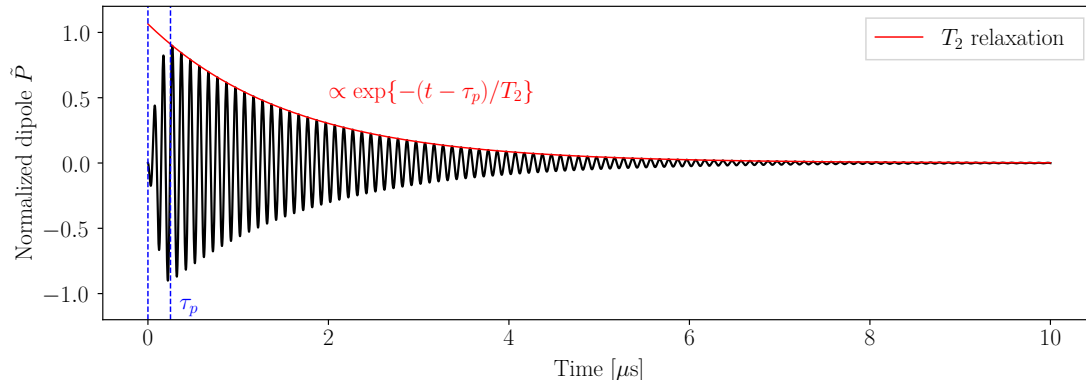


Fig. 2.4. Simulation of the normalized dipole driven by a $\pi/2$ -pulse with a pure dephasing term $T_2 = 10/\Omega_R$ and a detuning frequency $\delta = \Omega_r/2$.

in its equilibrium initial conditions, that is $u = 0$, $v = 0$ and $w = w_0 = 1$. Then, for $0 \leq t < \tau_p$, the molecules are illuminated with the near-resonant microwave radiation which drives the system into *transient absorption*, that is a displacement of the population w towards the higher energy state $|b\rangle$ and the emergence of a macroscopic polarization P , which can indeed be observed ramping up on the interval $[0, \tau_p[$ of Fig. 2.4. Finally, for $t \geq \tau_p$, the light is switched off (i.e., $\Omega_R = 0$) and the molecular system enters in a *transient emission* regime where the dynamics of the system are now solely steered by T_2 and δ . As seen in Fig. 2.4, the T_2 terms in the equations 2.11(a-b) induce an exponential decay of the envelope of the polarization $\tilde{P}$.

In NMR, the transient emission is also referred to as the *free induction decay* (FID). For both NMR or MW emission spectroscopy, the free induction decay is crucial as it actually *is* the signal that is detected. For the former method, the rotating macroscopic magnetization can be detected with the currents induced in a coil placed nearby the ensemble of spins (thanks to Faraday’s law), while the latter method directly detects the EM wave radiated by the rotating macroscopic electric dipole of the molecular gas.

It is worth noting that the example described above justifies the two-fold requirements for any MW emission spectrometer. One is to bring the molecular system out of equilibrium through transient absorption, and the second is to detect the subsequent molecular free induction decay.

Even though representing the molecular system evolution through the polarization $\tilde{P}$ of Fig. 2.4 is convenient to understand the signals that one should expect to detect in practice (e.g., on the oscilloscope), it does not allow to grasp the full picture of its dynamics, especially if the EM pulse excitation sequence becomes more complex. In the following, the Bloch sphere representation [16] is implemented as it tracks the evolution of (u, v, w) in $\mathbb{R}^3$. To this end, we define the Bloch vector

Θ , the driving vector Ω and the relaxation matrix Γ , written as [17]:

$$\Theta = \begin{pmatrix} u \\ v \\ w \end{pmatrix} \quad \Omega = \begin{pmatrix} \Omega_R \\ 0 \\ \delta \end{pmatrix} \quad \Gamma = \begin{pmatrix} 1/T_2 & 0 & 0 \\ 0 & 1/T_2 & 0 \\ 0 & 0 & 1/T_1 \end{pmatrix} \quad (2.13)$$

which allows to rewrite the optical Bloch equations 2.11 as [7]:

$$\dot{\Theta} = \Theta \times \Omega - \Gamma(\Theta - \Theta_0) \quad (2.14)$$

with $\Theta_0 = (0, 0, w_0)$. In Fig. 2.5, the same $\pi/2$ -pulse simulation as in Fig. 2.4 is displayed, but this time in the Bloch sphere representation. In this picture, the Bloch vector Θ follows the blue dots trajectory over time (three blue Θ vectors are added to emphasize particular states of the Bloch vector at given times) while the two red vectors represent the two states of the driving vector Ω for $t < \tau_p$ and $t \geq \tau_p$. Starting at $t = 0$, the Bloch vector is given by $\Theta(0) = \Theta_0 = (0, 0, 1)$. Then,

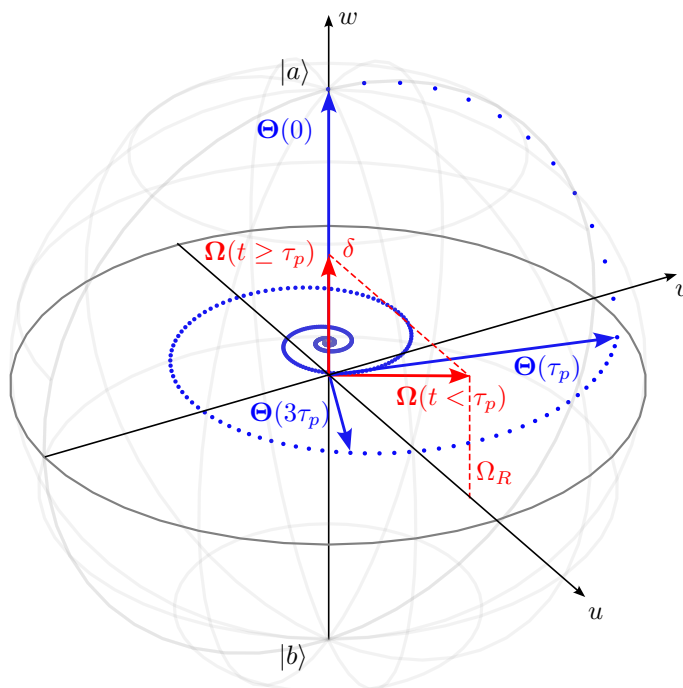


Fig. 2.5. Bloch sphere representation of $\pi/2$ -pulse with a pure dephasing term $T_2 = 10/\Omega_R$ and a detuning frequency $\delta = \Omega_r/2$.

under the action of the driving vector $\Omega(t < \tau_p) = (\Omega_R, 0, \delta)$, the Bloch vector begins to precess around Ω and falls towards the equatorial plane at a rate $|\Omega|$ for $t < \tau_p$. At $t = \tau_p$, the projection of Θ onto the uv -plane has a maximum magnitude $\sqrt{u(\tau_p)^2 + v(\tau_p)^2}$, hence the maximum polarization $\tilde{P}(\tau_p)$, meanwhile, the radiation is switched off instantaneously such that $\Omega(t \geq \tau_p) = (0, 0, \delta)$. The Bloch vector now evolves freely in the uv -plane (i.e., $\dot{w} = 0$) and rotates clock-wise around w at a rate δ , while the magnitude of the uv -projection of Θ decays towards the origin, driven by the relaxation rate $1/T_2$.

If one was not convinced that the dipole $\tilde{P}$ of Eq. 2.12 oscillates at the transition resonant frequency ω_{ab} , we must remember that the uv -plane is defined as the frame rotating in the trigonometric direction with the velocity of the excitation radiation ω . Since the Bloch vector rotates in the anti-trigonometric direction at a rate δ around the w -axis, then, by the addition law of velocities, the dipole must oscillates at a frequency $\omega - \delta$ which by definition is equal to ω_{ab} .

2.1.4 Chirped-pulses and linear fast passage

So far, only pulses whose frequency is kept constant throughout the light-molecules interaction duration have been considered, i.e., $\dot{\delta} = 0$. As one shall see in the next section, searching for molecular transitions with such narrowband pulses can become time consuming. The MW spectroscopy technique presented in this thesis allows to circumvent the constant frequency pulses limitation and is based on the theoretical grounds established by McGurk *et al.* [18].

In their work, they demonstrate the possibility of polarizing a molecular transition with an excitation pulse where the detuning frequency $\delta(t)$ is linearly swept, starting from $\delta(0) = \delta_i < 0$ at the beginning of the pulse, to $\delta(\tau_p) = \delta_f > 0$ at the end of the pulse. In practice, sweeping δ across the molecular transition is achieved either by sweeping the rotational transition frequency via Stark effect while keeping the microwave radiation frequency constant (as originally performed in [18]) or by keeping the transition frequency ω_{ab} constant and linearly sweeping the microwave radiation. The microwave excitation pulses employed in the latter technique are known as chirped-pulses or simply chirps; the remaining of this section is dedicated to their study.

To produce a chirped-pulse, the instantaneous frequency of the MW pulse $\omega(t)$ must be swept at a constant sweep rate denoted α such that $\dot{\omega}(t) = \alpha$, with the initial condition $\omega(0) = \omega_i$. The instantaneous frequency of the pulse thus reads as:

$$\omega_t = \omega_i + \alpha t \quad \text{for} \quad 0 \leq t < \tau_p \quad (2.15)$$

If the microwave chirped-pulse is written as:

$$\mathbf{E}^{(e)}(t) = E^{(e)}(t) \cos(\phi(t)) \hat{\mathbf{e}}_y \quad (2.16)$$

Then, the instantaneous phase $\phi(t)$ of the oscillating E-field is defined as:

$$\phi(t) = \int_0^t \omega_i + \alpha t' dt' = \omega_i t + \frac{\alpha t^2}{2} \quad (2.17)$$

It follows from the equations above that the final frequency of the chirp is given by $\omega_f = \omega(\tau_p) = \omega_i + \alpha \tau_p$. To gain some intuition about the chirped-pulse excitation of a molecular transition, a conceptual representation (not a simulation) of a typical chirped-pulsed excitation and detection experiment is illustrated in Fig. 2.6. As considered earlier, the rotational transition located at the frequency ω_{ab} is polarized as the MW chirped-pulse passes through the two-level molecular gas. We must set the chirp such that $\omega_i < \omega_{ab} < \omega_f$. The experiment begins when the chirped-pulse

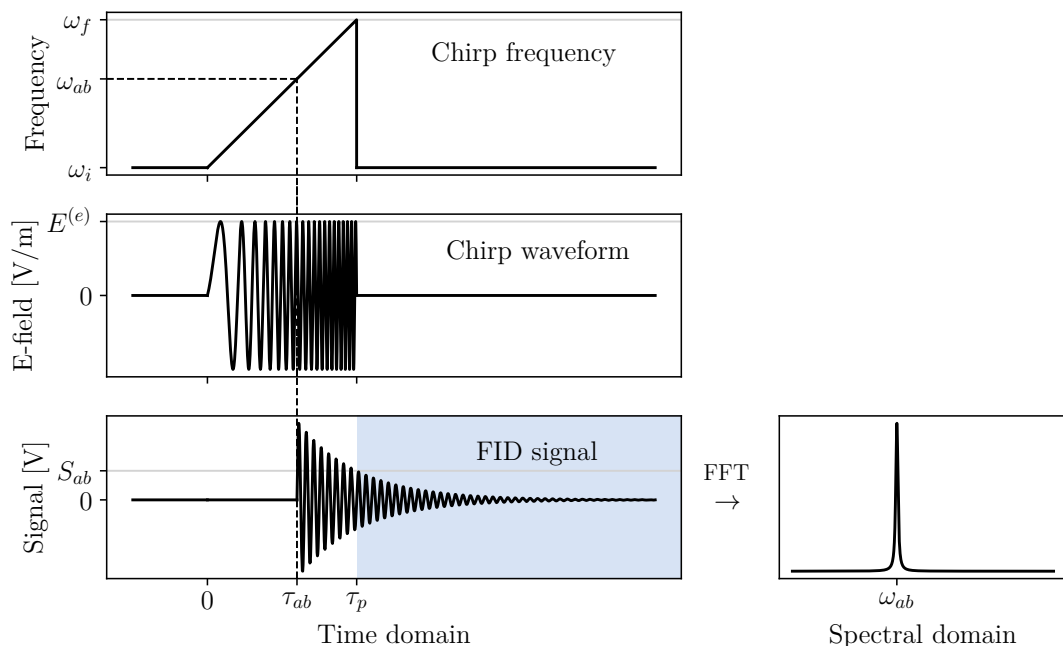


Fig. 2.6. Conceptual representation of the transient emission induced by a chirped-pulse.

is initiated at $t = 0$. In the top panel of fig. 2.6, the instantaneous frequency ramp of Eq. 2.15 is shown while the corresponding chirp signal of Eq. 2.16 is depicted in the middle panel of the same figure. When the chirp frequency ω approaches ω_{ab} , the molecular system is brought into resonance and transient absorption begins to occur which leads to the emergence of macroscopic polarization of the molecular sample, as developed earlier for constant frequency pulses. Right after the transient absorption, the molecular system is taken out of resonance as the frequency of the chirp ω continues its ascent towards ω_f . The molecular sample is thus left in a transient emission regime and emits its free induction decay signal, as shown in the bottom panel of Fig. 2.6.

Once the chirp has been switched off, for $t \geq \tau_p$, the FID signal can finally be measured and recorded by a detection instrument, where the strength of the measured FID signal is proportional to S_{ab} . It is important to notice that the FID signal cannot be measured before τ_p as the very powerful excitation chirped-pulse would simply corrupt any measurements before that time and even possibly damage the sensitive detection instrument. This last observation is emphasized in the bottom panel of Fig. 2.6 where the allowed detection temporal window is overlaid in light blue. Finally, the detection window is digitally Fourier transformed with the FFT algorithm and gives the molecular spectrum where the rotational transition line is precisely centered on ω_{ab} , in the frequency domain. In order to match the transition frequency with the oscilloscope bandwidth, down-conversion with a mixer and local oscillator can sometimes be implemented. This is the case in this work.

It is worth noting that Fig. 2.6 encapsulates all the core characteristics of the chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy technique: a molecular sample is excited by a microwave chirped-pulse and detected with a time-domain measurement which is subsequently Fourier transformed into a

molecular spectrum.

Before moving on to the development of the CP-FTMW instruments, we must dive deeper into how a chirped-pulse induces transient emission in the molecular sample and identify the two polarization regimes that can occur. To do this end, the Bloch sphere representation is used once again in Fig. 2.7 to present two identical chirped-pulse simulations, which only differ by their Rabi frequency (Ω_R is 20 times larger in Fig. 2.7a than in Fig. 2.7b). In both cases, the chirped-pulse has a sweep rate α and a duration τ_p which is small compared to the relaxation times (i.e., $\tau_p \ll T_1, T_2$) such that the relaxation processes can be neglected. Also, the molecular transition is assumed to lie at the center of the chirp (that is $\tau_{ab} = \tau_p/2$) which means that the initial and final detuning frequency are linked by the relation $\delta_f = -\delta_i$. The initial conditions are set by $\Theta(0) = \Theta_0 = (0, 0, 0.8)$.

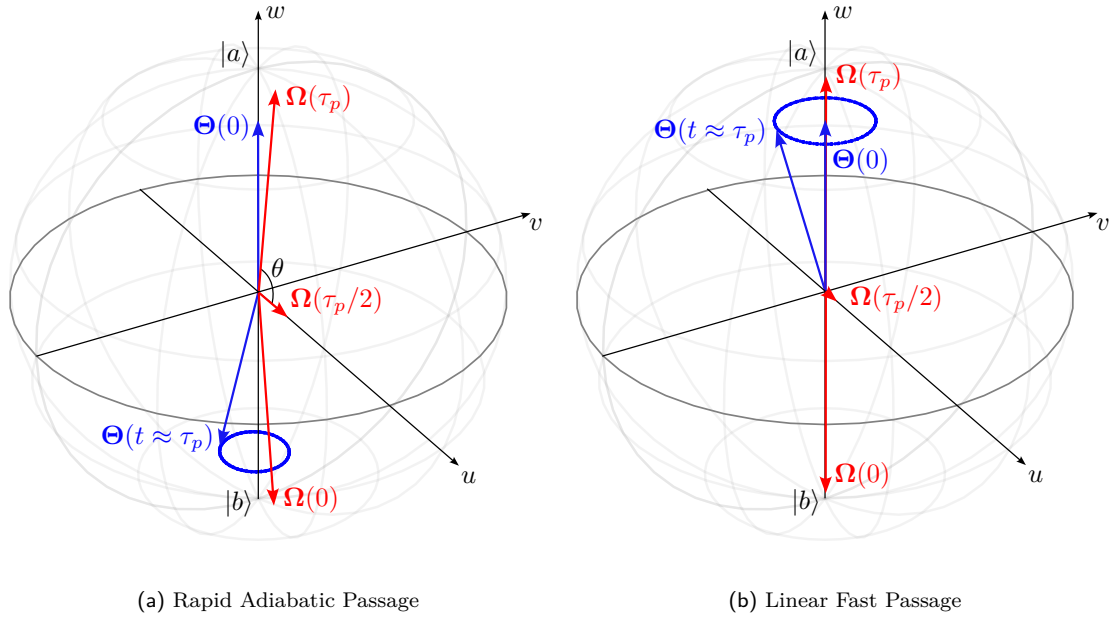


Fig. 2.7. Two identical simulations of a chirped-pulse in the Bloch sphere representation, where no relaxation processes are considered. The Rabi frequency is 20 times larger in panel (a) than in panel (b).

In both figures Fig. 2.7a and Fig. 2.7b, the driving vector is indicated in red $\Omega(t)$ for t equal to 0, $\tau_p/2$ and τ_p while the Bloch vector is given in blue at $t = 0$ and for $0.99\tau_p \leq t < \tau_p$, with the precession orbit of the Bloch vector $\Theta(t \approx \tau_p)$. In Fig. 2.7a, we observe that the Bloch vector has undergone an almost complete population inversion, that is $w(\tau_p) \approx -w(0)$ while the Bloch vector of Fig. 2.7b has not significantly evolved in terms of population where $w(\tau_p) \approx w(0)$. The large discrepancy between those two outcomes is related to the speed at which the driving vector is toggled between $t = 0$ to $t = \tau_p$ and is given by the time derivative of the elevation angle θ formed between the driving vector Ω and the u -axis:

$$\frac{d\theta}{dt} = \frac{d}{dt} \arctan \left(\frac{\delta}{\Omega_R} \right) = \frac{1}{\Omega_R + \delta^2/\Omega_R} \frac{d\delta}{dt} = \frac{\alpha}{\Omega_R + \delta^2/\Omega_R} \quad (2.18)$$

At resonance, the angular speed of the driving vector simplifies into $\dot{\theta} = \alpha/\Omega_R$ and two cases can arise from there. If $\dot{\theta} \ll \Omega_R$, then $\Omega_R^2/\alpha \gg 1$ which means that the

Bloch vector precesses around the axis of Ω much faster than $\dot{\theta}$ and thus manages to keep precessing tightly around Ω as it passes through resonance to finally reach population inversion at the final detuning. Indeed, the final population difference in this simulation is $w(\tau_p) = -0.98w(0)$. This case is known as the rapid adiabatic passage (RAP) and is depicted in Fig. 2.7a where $\Omega_R^2/\alpha = 8.4$.

On the other hand, if $\dot{\theta} \gg \Omega_R$ at resonance, then $\Omega_R^2/\alpha \ll 1$ and the Bloch vector precesses around Ω much slower than the rate at which Ω passes through resonance. Therefore, Θ fails to follow Ω and rapidly stalls near its initial population difference, which is given in this simulation by $w(\tau_p) = 0.97w(0)$. This case is referred to as the linear fast passage (LFP) and is illustrated in Fig. 2.7b where the condition $\Omega_R^2/\alpha \ll 1$ is known in this case as the weak field limit, and is satisfied with $\Omega_R^2/\alpha = 0.02$.

2.2 Development of the CP-FTMW technique

2.2.1 Background

The spectrometers that perform time-domain measurements of molecular transient emission (as described in the previous section) are known as Fourier transform microwave spectrometers (FTMW), and the first occurrence of such an instrument was reported in 1955 by Romer and Dicke. [19] Since then, FTMW techniques have gained a lot of interest among the microwave spectroscopy community thanks to the inherent high sensitivity of the background-free detection and high resolution of the Fourier transformed FIDs.

In 1981, Balle and Flygare invent the first cavity-FTMW design where a molecular beam is introduced via supersonic expansion (described in chapter 5) into a Fabry-Perot microwave cavity, coupled to a pulsed microwave source. [20, 21] The Fabry-Perot cavity allows for the passive amplification of the excitation microwave pulse and the molecular transient emission, which therefore provides an outstanding sensitivity. The cavity however reduces the bandwidth of the overall instrument down to ~ 1 MHz which is impractical and time consuming if one wants to search for unknown transitions or perform a broadband survey of a molecular spectrum. Indeed, a scan of few hundreds MHz typically take up to one hour to complete, due to the mechanical adjustment of the Fabry-Perot cavity required to tune the central resonant frequency. [22]

2.2.2 First design of the CP-FTMW spectrometer

Invented in 2006 by the Pate lab at the University of Virginia, the chirped-pulse Fourier transform microwave (CP-FTMW) is the second FTMW instrument to provide another major leap forward in the field of microwave spectroscopy, after the invention of the cavity-FMTW. [1, 2]. Its first design is shown in Fig. 2.8 as reproduced from reference [23]. The spectrometer is divided in three modules with the chirped-pulse generation and amplification module, the interaction region where the molecules interact with the microwave radiation and the FID detection

module where the FID is amplified and digitized by a fast oscilloscope.

To survey the 8-18 GHz region of the molecular spectra, a 1 μ s phase-reproducible chirped-pulse of 10 GHz bandwidth is generated by a 20 GSa/s arbitrary waveform generator (AWG) and up-converted by mixing with a phase-locked oscillator (PLDRO). The up-converted chirp is then amplified by a traveling wave tube

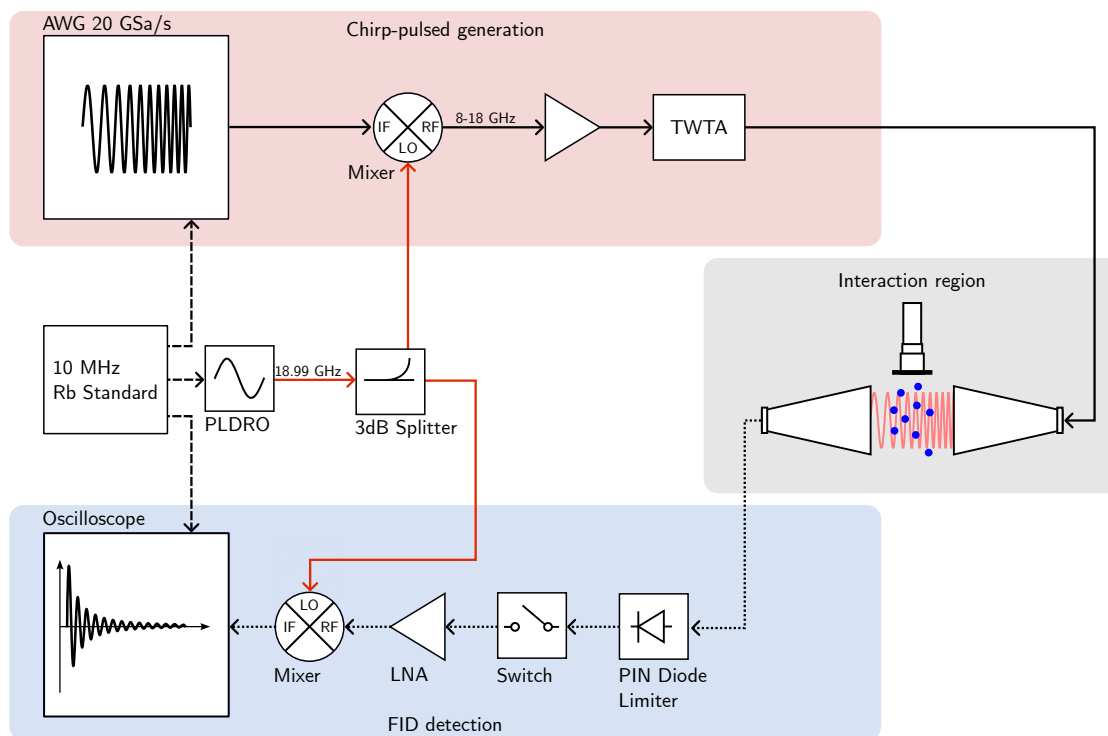


Fig. 2.8. Original CP-FTMW spectrometer design, reproduced from [23]. The three main modules of this instrument are the 10 GHz chirped-pulse generation and amplification (in red), the interaction region between the microwave chirp and the molecules (in gray) and finally the amplification along with the detection of the subsequent free induction decay (in blue). The signals are: chirped-pulse (solid black lines), FID signal (dotted black lines) LO signal, (red lines) and 10 MHz phase-lock signals (dashed lines.)

amplifier (TWTA) capable of delivering up to several kilowatts of peak power. The chirped-pulse then enters via standard gain horn antenna in the microwave-molecule interaction region and induces the polarization of the molecular sample. At the detection side, the sensitive low noise amplifier (LNA) is protected from the powerful chirped-pulse with a PIN diode limiter and a single pole single throw (SPST) switch. During transient emission (i.e. when the excitation pulse is over), the switch is closed and the FID signal collected by the other horn antenna is able to be amplified by the LNA, down-converted back into the 10 GHz baseband and digitized by the oscilloscope. The last crucial aspect of this design is the use of a low phase noise 10 MHz rubidium reference clock to phase lock the clocks of the AWG, the oscilloscope and the PLDRO. This allows to perform multiple consecutive excitation/detection experiments and collect multiple FID acquisitions which are coherent in phase. Those FID acquisitions can then be co-added and averaged before the Fourier transform which results in the lowering of the spectrum noise floor and thus improves the overall sensitivity of the spectrometer. [24] Typically 10^6 FIDs are averaged for the obtention of one spectrum.

It is clear that such a design would not have been possible without the technical advances that led to the commercialization of the high-end AWG, the TWTA or the fast oscilloscope, but by essence, this technique is mostly relying on the chirped-pulse theory, derived by McGurk *et al.* long before the invention of CP-FTMW instrument. Indeed, Pate *et al.* used the fast passage theory [18] to determine the signal strength S_{ab} obtained with the CP-FTMW spectrometer in the weak field limit, which follows the relation:

$$S_{ab} \propto \omega_{ab} \mu_{ab}^2 E^{(e)} \Delta N_0 \left(\frac{\pi}{\alpha} \right)^{\frac{1}{2}} \quad (2.19)$$

where ΔN_0 is the total population difference, that is $\Delta N_0 = N_a - N_b = N w_0$. It is worth noting that the weak field limit $\Omega_R^2/\alpha \ll 1$ is a reasonable assumption with a chirp that spans 10 GHz over 1 μ s, and thus it can be assumed that $\Delta N \approx \Delta N_0$, even though it has been reported that powerful TWTA in some cases may not respect this condition [25]. The main consequence of Eq. 2.19 is that for chirped-pulse with a fixed duration τ_p and broadcast with a magnitude $E^{(e)}$ fixed by the peak power of the last amplifying stage of the chirped-pulse generation module, the strength of the signal falls as the inverse square root of the chirped-pulse bandwidth. If one wanted to use instead a Fourier-transform-limited (FTL) pulse (e.g., a sinus cardinal pulse) with the same broadcast peak power, then the signal strength would fall linearly with the bandwidth.

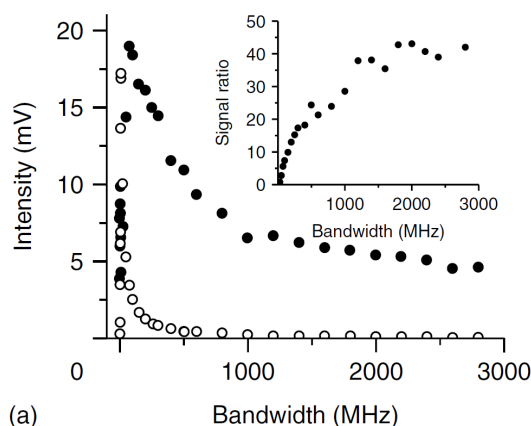


Fig. 2.9. This figure is taken from [23]. Molecular signal intensities obtained with a chirped-pulse (black dots) and with a FTL pulse, respectively. The inset is the signal ratio of the chirped-pulse with respect to the FTL pulse.

In Fig. 2.9, Shipman *et al.* [23] show the molecular signal strengths obtained upon excitation with a chirped-pulse (black dots) and with a FTL pulse (white dots) as a function of the excitation bandwidth. The peak power is fixed for both pulses and the duration of the chirped-pulse is held constant. As the bandwidth of both pulses is increased, the molecular signal obtained with the chirped-pulse falls as $1/\sqrt{B}$, where the B is the bandwidth while the FTL pulse falls as $1/B$. Therefore, the advantage of using the chirped-pulse over the FTL pulse scales as $\sqrt{B}$, which is indeed the trend that is observed in the inset of Fig. 2.9.

2.2.3 Evolution of the CP-FTMW spectrometer

In 2013, Finneran *et al.* demonstrate the possibility of replacing the expensive and bulky arbitrary AWG by a direct digital synthesizer. [3] Previously used in radar applications, [26] the DDS are digital integrated circuits capable of producing digital linear frequency ramps which are converted into an analog chirped-pulse via a digital-to-analog converter (DAC). A detailed description of the operation principles of the DDS is given in the following chapter.

In Table 2.2, it is shown that the AWG used in the original CP-FTMW design display comparable performances in terms of sample rate and resolution. Moreover, Finneran *et al.* showed that the spectral purity of the DDS output was similar to the one of the AWG. They also demonstrated that DDS does not introduced additional phase noise by showing that the $\sqrt{N}$ scaling of the SNR with respect to the number averages N was achieved in both configurations.

Table 2.2: Comparison between the arbitrary waveform generator (AWG) Tektronix AWG710B used in Ref. [2] and the direct digital synthesizer (DDS) Analog Devices AD9914 implemented in Ref. [3].

	Sample rate [GSa/s]	Resolution [bit]	Price [€]	Weight [kg]	Size [m ³]	Power consumption [W]
AWG	4.2	8	> 10k	> 14	0.04	>100
DDS	3.5	12	~ 1k	≪ 1	$1.5 \cdot 10^{-4}$	< 3

However, the DDS is far more advantageous if one wants to optimize the cost, the weight, the footprint and the power consumption of the instrument. The DDS-based CP-FTMW is thus a design of choice for *in situ* applications. [3] To reduce even further the overall footprint of the spectrometer, it is possible to replace the fast oscilloscope by an analog-to-digital (ADC) card (also referred to as digitizer) [3, 5] or by a USB portable oscilloscope [4]. The down side of such upgrades is the reduction of the detection bandwidth compared to high-end large-bandwidth oscilloscopes.

Bandwidth-limited digitizers can nonetheless acquire large broadband molecular spectra by segmenting the total desired bandwidth B and tuning the down-conversion LO to bring each segment within the baseband of the digitizer. In theory, based on equation 2.19, the acquisition time required to collect a molecular spectrum over a given bandwidth B and a fixed sensitivity is independent of the number of segments considered to cover the bandwidth B . Indeed, if B is divided into N segments, then according to Eq. 2.19, the molecular sensitivity in each segment scales by $\sqrt{N}$, requiring N fewer acquisitions per segment to achieve the same sensitivity set in the unsegmented case (since the sensitivity also scales with the square root of the number of averaged acquisitions). But since N segments need to be collected in total to recover the full bandwidth B , then the benefit of segmenting the bandwidth breaks even; no difference in measurement time occurs.

If performed the right way, segmenting the bandwidth can reduce the cost of the instrument by half without sacrificing on the acquisition time. [27] The most optimal scheme to acquire a segmented broadband spectrum with bandwidth-limited

digitizers have been derived by Neill *et al.* and is referred to as the “segmented chirped-pulse Fourier transform” technique. [28] In Fig. 2.10, an illustration of the spectrogram depicts the instantaneous frequency of the chirp and the LO used for down-conversion, over the course of one acquisition. The segmented CP-FT exploits a fast-switching LO frequency to record the N segments of the full bandwidth in one time-domain acquisition of duration t , which is thus N times larger than its unsegmented counterpart. As seen in Fig. 2.10, the LO frequency is stepped between each segment to down-convert the segment currently excited by the chirp to the baseband of the digitizer. Thanks to sensitivity gain per segment described in the previous paragraph, the segmented CP-FT requires N fewer acquisitions. While it does not change the measurement time (as stated in the previous paragraph) it does reduce however the overhead time in data processing inherent to each acquisition by a factor of N , which in turn increase the data acquisition rate of the instrument. The optimum number of segments is given by the highest number possible that still satisfy the weak field limit.

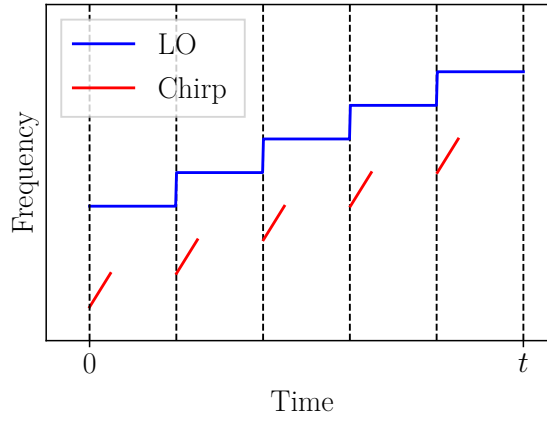


Fig. 2.10. Spectrogram illustration of the chirp and the LO signal over one segmented CP-FT acquisition of duration t . Reproduced from [28].

Chapter 3

Design and characterization of the CP-FTMW spectrometer

The design of the CP-FTMW spectrometer developed during this project is displayed in Fig. 3.1. Following the signal path, the instrument can be broken down in three main modules with first the excitation arm which produces the excitation pulse, followed by the waveguide cell where the molecules are confined to interact with the incident electric field and finally the detection arm which captures the subsequent time domain molecular emission with a fast digitizer. The timing sequence required to perform an excitation-detection experiment with the spectrometer is controlled by the digital delay generator (DDG). Moreover, the excitation and detection modules are clocked by a low phase noise 10 MHz frequency reference provided by the GPS disciplined oscillator (GPSDO) to generate phase-reproducible chirp-pulses and molecular FID acquisitions.

In the following, the main modules of the instrument are reviewed and characterized as a mean to extract the figures of merit and the expected performances of this CP-FTMW spectrometer design. We also provide the detailed timing scheme of the spectrometer which has a crucial impact on the instrument sensitivity.

3.1 Excitation module

The excitation module is composed of three stages: the excitation pulse generation, the upconversion and the amplification stages. The combination of those three stages allows to produce a 1 μ s chirped pulse which spans a 200 MHz bandwidth, tunable between 10 and 18 GHz (i.e., over the Ku-band).

3.1.1 Direct Digital Synthesis

As discussed earlier, one of the key improvement on the original CP-FTMW design of Pate *et. al* in 2008, is the replacement of the bulky and expensive arbitrary waveform generator (AWG) by a direct digital synthesizer (DDS), as it was first demonstrated by Finneran *et. al* in 2013. The DDS implemented in this setup (AD9915 evaluation board) is similar to the DDS used in Ref. [3] (ADD9914

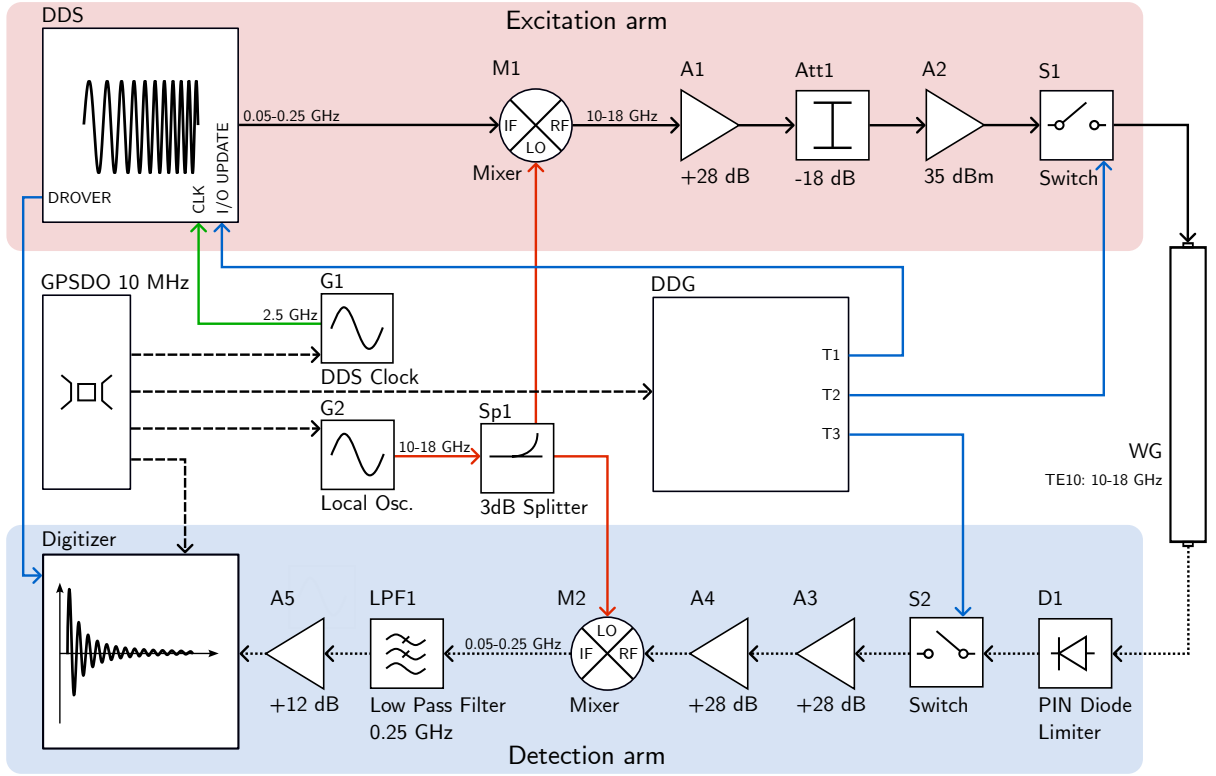


Fig. 3.1. The excitation arm is presented in the red area while the detection arm is presented in the blue area. The molecular sample is placed in the waveguide (WG). **The signals are:** excitation signal path (solid black lines), molecular signal path (dotted black lines), TTL signals (blue lines), 10 MHz external clock signal (dashed lines), local oscillator signal (red lines), DDS clock (green line). **The components are:** AD9915/PCBZ (DDS), wideband frequency mixer ZX05-24MH-S+ (M1, M2), wideband microwave amplifier ZX60-183A-S+ (A1, A3, A4), BW-S10W2+ (-10 dB) and BW-S8W2+ (-8 dB) (Att1), power amplifier ZVE-3W-183+ (A2), SPDT non-reflective switch HMC347 (S1, S2), rectangular waveguide WR62/WG18/R140 (WG), PIN diode limiter ACLM-4537 (D1), low pass filter SLP-550+ (LPF1), ZX60-14012L-S+ (A5), TiePie Handyscope HS5-540XM (Digitizer), 10 MHz reference clock Fury Jackson Labs Technologies (GPSDO), 2.5 GHz clock Valon 5008 (G1), local oscillator Valon 5015 (G2), 3dB power splitter ZX10-2-183-S+ (Sp1), digital delay generator BNC 745 (DDG).

evaluation board). Most of the information presented below is based on the AD9915 datasheet. [29]

Commercialized by the Analog Device company, the AD9915 chip embeds a 2.5 GSPS DDS along with a 12 bit D/A converter (DAC). To operate at its nominal system frequency f_{CLK} of 2.5 GHz, an external clock is provided to the DDS by the Valon 5008 synthesizer, as shown in Fig. 3.1. The key feature of the AD9915 for our application is its digital ramp generator (DRG) module which allows the DDS to produce a chirp signal whose frequency is linearly swept over any frequency interval $[f_{min}, f_{max}]$, between DC and $0.4f_{CLK} = 1$ [GHz] (that is, an upper bound slightly below the Nyquist frequency $f_{CLK}/2$).

Digital Ramp Generator & Direct Digital Synthesis

Since the DRG is a digital module, all its parameters are defined by integers stored in registers and gain physical units by means of the system frequency f_{CLK} . For instance, f_{min} and f_{max} are defined by 32-bit unsigned integer “frequency tuning words” (FTW) such that:

$$f_{min} = \left(\frac{FTW_{min}}{2^{32}} \right) f_{CLK} \quad f_{max} = \left(\frac{FTW_{max}}{2^{32}} \right) f_{CLK} \quad (3.1)$$

where FTW_{min} and FTW_{max} are the digital frequency ramp lower and upper limits, respectively. Also, the frequency ramp has discrete time steps Δt and frequency steps Δf given by the following equations:

$$\Delta t = \frac{24P}{f_{CLK}} \quad \Delta f = \left(\frac{M}{2^{32}} \right) f_{CLK} \quad (3.2)$$

where P is the 16-bit unsigned integer “digital ramp rate” and M is the 32-bit unsigned integer “rising ramp step size”. As shown in Fig. 3.2, the four aforementioned integer parameters allows to fully characterize the digital frequency ramp $f_c[n]$ produced by the DRG and sent to the DDS as a frequency command. The DDS then converts this frequency command $f_c[n]$ into a discrete-time chirp signal $s[n]$, which is finally transformed into the desired continuous linear chirp $s(t)$ by the DAC. It is worth noting that while the DDS is strictly speaking a module in the larger circuit of Fig. 3.2, we often refer to the full circuit as the “DDS”.

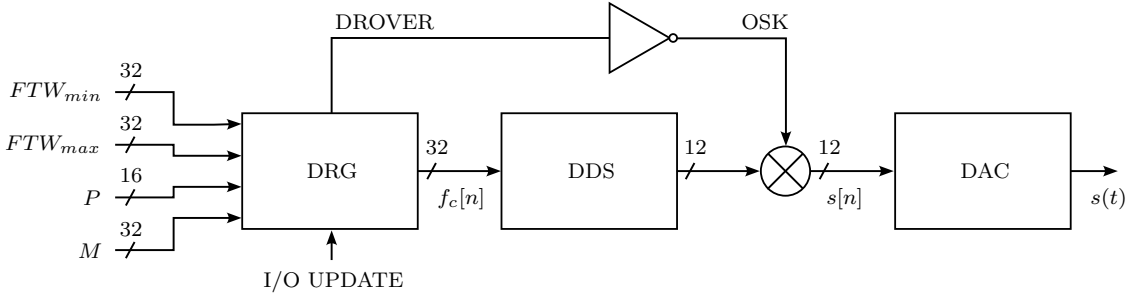


Fig. 3.2. Digital block representation of the internal modules and signals involved in the chirp generation of the DDS AD9915.

Following the equations above, the digital frequency ramp signal $f_c[n]$ drives a linear chirp of duration t_c , which reads as follows:

$$t_c = \frac{(f_{max} - f_{min})}{\Delta f} \Delta t = \frac{(FTW_{max} - FTW_{min})}{M} \frac{24P}{f_{CLK}} \quad (3.3)$$

The slope of this linear chirp is defined as the sweep rate α and is expressed as:

$$\alpha = \frac{\Delta f}{\Delta t} = \frac{M}{3 \cdot 2^{35} P} f_{CLK}^2 \quad (3.4)$$

Which in turn allows us to define the instantaneous frequency $f_c(t)$ of the chirp signal $s(t)$, given by:

$$f_c(t) \approx \alpha t + f_{min} \quad \text{with} \quad 0 \leq t \leq t_c \quad (3.5)$$

where we assumed $\Delta f \ll (f_{max} - f_{min})$ and $\Delta t \ll t_c$.

Timing of the chirp generation

In Fig. 3.3, we illustrate the timing diagram of a chirp generation in normal operation. The output signal $f_c[n]$ of the DRG and $s(t)$ of the DAC are depicted along with the DDS logic signals of Fig. 3.2 which have not been covered yet. As suggested in Fig. 3.1, the DDS is triggered by the DDG when the latter issues a pulse via its T1 output to the I/O UPDATE input of the DDS. Then, the DRG immediately initiates a digital frequency ramp of duration t_c and sends while the actual analog chirp $s(t)$ produced by the DAC.

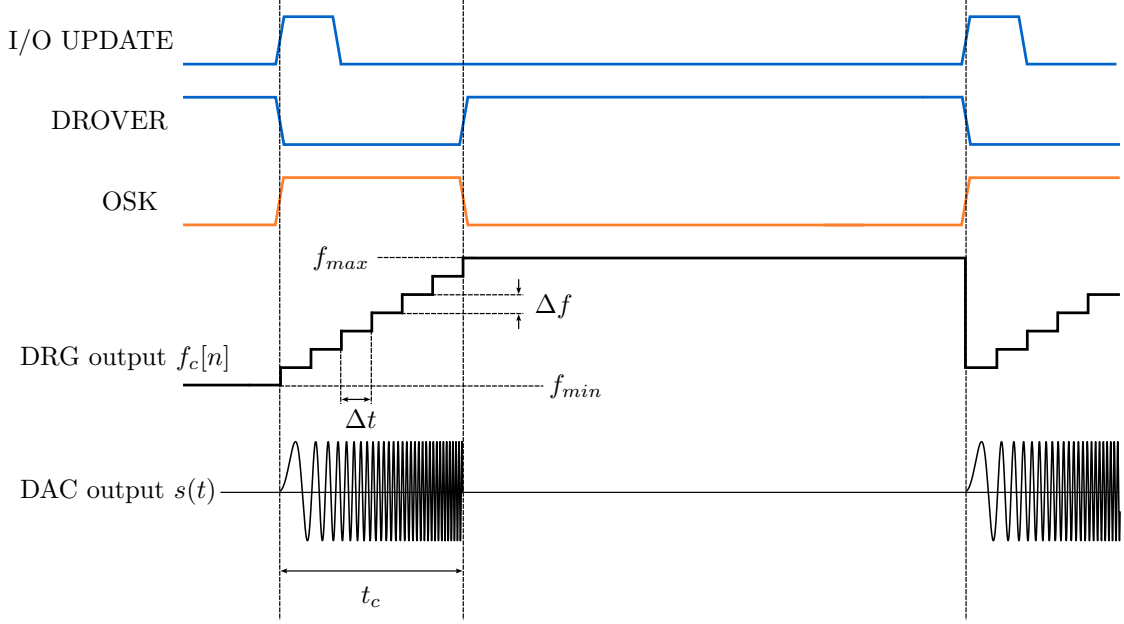


Fig. 3.3. Timing diagram of the digital ramp generator in normal operation. The blue traces are I/O signals of the DDS, the orange OSK signal is used internally in the DDS to modulate the amplitude of the DAC output. The last two traces represent the outputs of the DRG and the DAC, respectively.

The DRG also provides a status signal named “digital ramp over” (DROVER) which is set to a logic 0 if a ramp is currently active and is set to a logic 1 otherwise. As depicted in Fig. 3.2, this status signal is used to modulate the amplitude of the digital chirp signal $s[n]$ via the “output shift keying” (OSK) pin. When set to a logic 1, OSK enables the full amplitude of the chirp signal and if OSK is set to a logic 0, then the chirp signal is suppressed. In practice, the DROVER signal is inverted by a custom logical inverter circuit and fed to the OSK pin such that $OSK = \overline{DROVER}$. This system allows to suppress the CW signal of frequency f_{max} that would otherwise remain at the end of every chirp and prevent the background-free detection of the FID signal. It is also worth noting that the DROVER signal is a reliable trigger for the digitizer (as shown in Fig. 3.1), as it guarantees that the digital frequency ramp is always in phase between multiple digitizer acquisitions.

Analog chirp analysis

To illustrate the full capabilities of the DDS, we display in the top panel of Fig. 3.4 a full 50 MHz to 1 GHz chirp over $\sim 12 \mu\text{s}$. This time domain acquisition has been performed with a high-end 40 GSa/s Agilent DSO7104A oscilloscope, which offers a Nyquist frequency of 20 GHz and an analog bandwidth of 8 GHz.

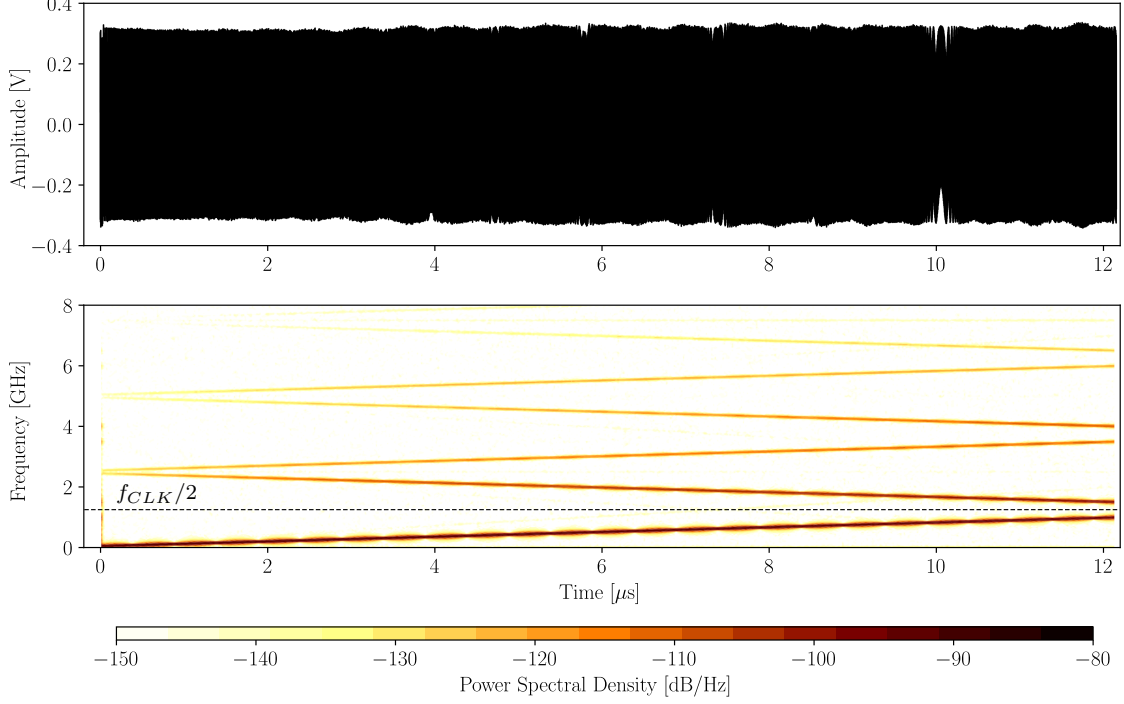


Fig. 3.4. Time domain

In the bottom panel of Fig. 3.4 we show the spectrogram of the 1 GHz chirp, where we took advantage of the large bandwidth of the oscilloscope to explore the super-Nyquist content (i.e., any spectral content above $f_{CLK}/2 = 1.250$ [GHz]). As one could expect, below $f_{CLK}/2$, the power spectral density (PSD) is focused on a sharp line which closely follows the instantaneous frequency $f_c(t)$ of the chirp and evolves with the same slope $\alpha \approx 5.2 \cdot 10^{13}$ [Hz $\cdot$ s $^{-1}$] as the frequency ramp generated by the DRG.

Above $f_{CLK}/2$, in the super-Nyquist region, we find the images of the chirp which extend over the full 8 GHz bandwidth of the oscilloscope. Those images are created by the *sample-and-hold* behavior of the DAC. In Fig. 3.5, we show that this D/A conversion technique can be modelled in the time domain as the convolution of the discrete-time chirp $s[n]$ and a gate function $g(t)$ which spans a width equal to the sampling period $T_S = 1/f_{CLK}$. In the Fourier domain, this convolution becomes:

$$\mathcal{F}\{s[n] * g(t)\} = S(\omega) \cdot G(\omega) \quad (3.6)$$

where the FT of $s[n]$ gives the periodic spectrum $S(\omega)$ (since $s[n]$ is discrete) and $G(\omega)$ is the FT of the gate function, written as:

$$G(\omega) = T_s \text{sinc}\left(\omega \frac{T_s}{2}\right) \quad (3.7)$$

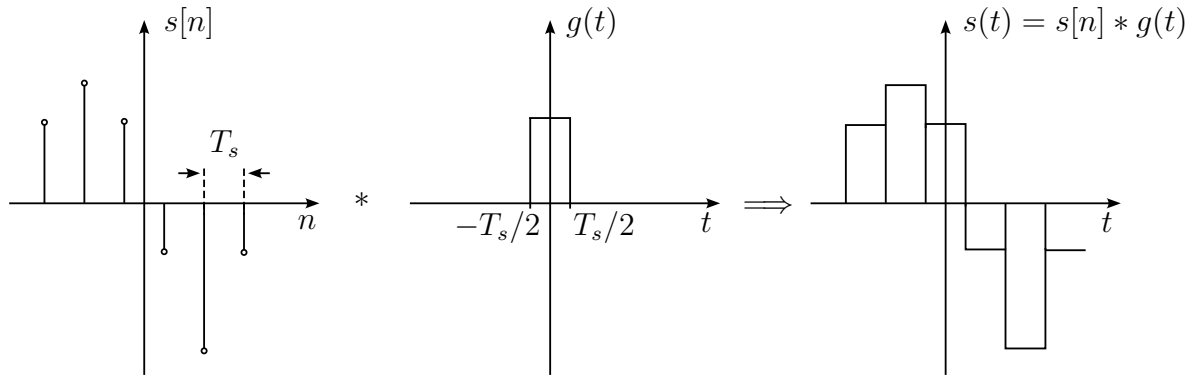


Fig. 3.5. Illustration of the *sample-and-hold* digital to analog conversion.

Therefore, what we observe in the spectrogram of Fig. 3.4 is the periodic spectrum of the discrete-time chirp $s[n]$, modulated by the envelope of the sinus cardinal of Eq. 3.7 which attenuates the PSD of the image lines as the frequency increases.

The same observations are made in the actual power spectrum of the full chirp, shown in Fig. 3.6. We find the baseband signal of interest between 0 and $f_{CLK}/2$ and its mirror image between $f_{CLK}/2$ and f_{CLK} . This spectrum is then repeated infinitely and modulated in magnitude by a $\text{sinc}(x)$ profile whose roots are multiple of f_{CLK} .

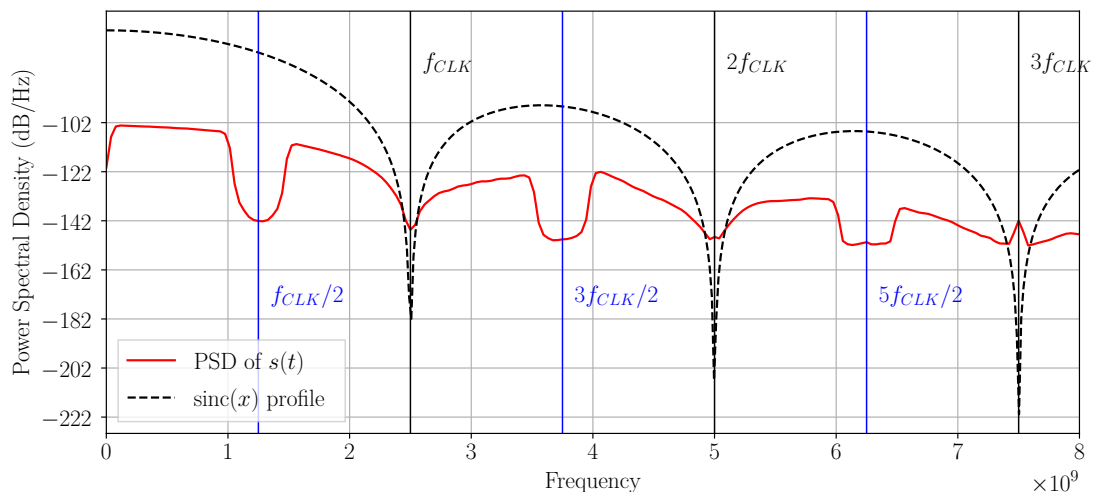


Fig. 3.6. Power spectral density of the chirp displayed in the top panel of Fig. 3.4.

While less intense than the baseband chirp, we must keep in mind that the chirp images may polarize unwanted transitions and should be filtered out with a low pass filter to ensure accurate measurements. The super-Nyquist may also be used to extend the bandwidth of the polarizing chirped-pulse. [30]

3.1.2 Upconversion

As stated previously, the maximum output frequency of the 2.5 GSPS DDS is limited by the near Nyquist frequency of 1GHz, that is well below the 10 GHz

cutoff frequency of the first propagating mode allowed in the waveguide static cell (i.e., the TE₁₀ mode). To move past this limitation, the excitation chirp is up-converted with a mixer from the intermediate frequency (IF) band, where the chirp typically spans a bandwidth f_c of 50-250 MHz, to the “radio frequency” (RF) band by mixing the chirp signal with the local oscillator (LO) signal of frequency f_{LO} .

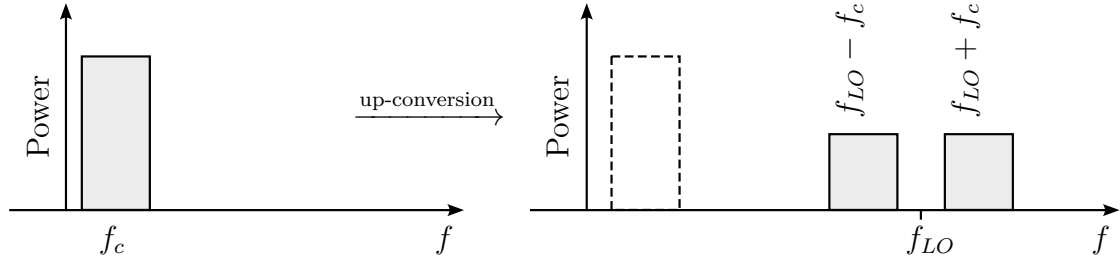


Fig. 3.7. Frequency domain illustration of the up-converted chirped-signal produced by the DDS with a swept bandwidth of f_c (typically 200 MHz)

As illustrated in Fig. 3.7, the up-conversion of the chirp, initially swept over a bandwidth f_c in the IF band, gives rise to a lower side band (LSB) located at $f_{LO} - f_c$ and an upper side band (USB) at $f_{LO} + f_c$ in the RF range. [31] We observe that both side bands can be used equivalently to probe a given molecular transition located in the RF frequencies. In this work, we mostly use the USB to probe the transitions, unless stated otherwise. Therefore, by an appropriate choice of f_{LO} in the 10-18 GHz frequency region, one can explore the full Ku-band with the USB of the up-converted chirp.

The up-conversion mixer (M1) used in the excitation module of Fig. 3.1 is a double balanced wideband frequency mixer, which requires to be driven by a 13 dBm signal at its LO port. This signal is provided by the Valon 5015 synthesizer (G2), which outputs a 16 dBm continuous wave (CW) signal of frequency f_{LO} (10-18 GHz). The signal is then split by the 3 dB power splitter (Sp1) to drive both M1 and M2 mixers with the same 13 dBm LO signal. In those conditions, the mixer M1 up-converts the 50-250 MHz chirp in the Ku-band with a 7 dB conversion loss, which is a typical value for a passive diode mixer. [32]

3.1.3 Amplification

Once the chirped pulse is up-converted, it must be amplified before entering the waveguide cell. Indeed, according to Eq. 2.19, the amplitude of the molecular emission signal scales linearly with the electric field amplitude $E(e)$ of the incident excitation chirped pulse. A maximum E-field is thus desired to improve the sensitivity of the instrument. In our setup, the maximum $E(e)$ achievable in the waveguide static cell is set by the peak output power of the power amplifier (A2).

With a gain of 35 dB, the power amplifier must receive a 0 dBm signal at its input port to reach the slightly saturated output power, below the 3 dB compression point at 35 dBm (~ 3 W). To match this power requirement, we inserted an attenuator (Att1) after the preamplifier (A2), as illustrated in Fig. 3.1. Indeed, by

adjusting the power level (with A2 and Att1) of the excitation chirp at the input port of the power amplifier, we take advantage of the full peak power of the PA, without generating too much intermodulation distortion (assuming that the 3 dB compression point is acceptable for our application).

3.2 Waveguide static cell

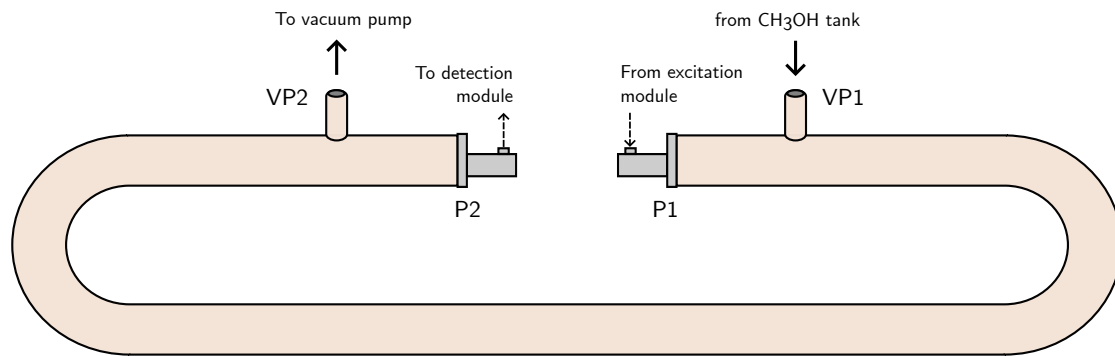


Fig. 3.8. Schematic of the U-shaped waveguide static cell.

The waveguide static cell is a standard WR62 rectangular waveguide, operating at room temperature and placed under vacuum. The waveguide is equipped with two vacuum ports VP1 and VP2, as shown in Fig. 3.8. VP2 connects the WG static cell to a vacuum turbomolecular pump, which is able to establish vacuum levels as low as $7 \cdot 10^{-4}$ mbar inside the waveguide cell. Once this vacuum level is reached, the molecular sample (e.g. methanol) is gradually introduced into the static cell by opening the valve of the molecular sample tank, connected to VP2. This process is stopped once the desired pressure is achieved (typically $\sim 10^{-2}$ mbar) and remains stable. At this stage, the waveguide static cell is ready for the experiment.

The two electromagnetic ports P1 and P2 of the waveguide are connected to the excitation and detection modules via WG-SMA adapters (depicted in gray in Fig. 3.8). The excitation chirp enters the waveguide in P1 and induces a macroscopic polarization of the molecular sample as soon as the instantaneous frequency of the chirp reaches the resonant frequency of the transition we are aiming to probe. After excitation, the FID signal emitted by the rotating molecules is transmitted through the P2 port, into the detection module.

The WR64 rectangular waveguide has dimensions $a = 15.7988$ [mm] and $b = 7.8994$ [mm] and therefore propagates the TE_{10} mode in a frequency band ranging from its cutoff frequency $f_{c,10} = c/2a = 9.488$ [GHz] to the cutoff frequency of the next allowed mode TE_{20} with $f_{c,20} = c/a = 18.976$ [GHz]. In this configuration, the electric field is polarized along the y -component of the waveguide, as shown in Fig. 3.9. If we assume perfect vacuum, no losses inside the waveguide and no reflected power at the input port, the electric field produced by the excitation module, inside the waveguide, is set by the following equation:

$$\bar{\mathbf{E}}^{(e)}(x, z) = -2j \sqrt{\frac{\omega \mu P^{(e)}}{ab \beta_{10}}} \sin\left(\frac{\pi x}{a}\right) e^{-j\beta_{10}z} \hat{\mathbf{e}}_y \quad (3.8)$$

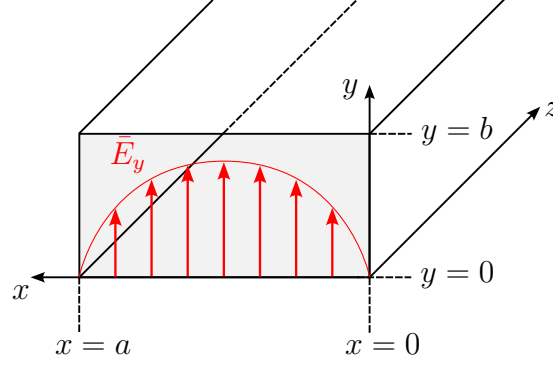


Fig. 3.9. Electric field representation for the TE_{10} mode inside the waveguide.

where β_{10} is the propagation coefficient for the TE_{10} mode and is defined as $\beta_{10} = \sqrt{(\omega/c)^2 - (\pi/a)^2}$. The strength of the electric field is proportional to the square root of the excitation power $P^{(e)}$ delivered by the power amplifier at the input port P1 of the waveguide, emphasizing further the critical role of the amplifying stage.

In Fig. 3.10, we computed the theoretical magnitude of the E-field inside the waveguide at $x = a/2$ and $z = 0$, for various frequencies and input powers, based on Eq. 3.8. In Fig. 3.10a, we present on the red trace the E-field that is achieved with the current power amplifier, capable of delivering an excitation power of 35 dBm. The maximum E-field is obtained at 10 GHz with $11 \cdot 10^3$ V/m. Also, on the blue trace of the same figure, we computed the E-field that would be obtained if the amplifier A2 was upgraded with a 40 dBm (10 W) power amplifier. With a value of $19.6 \cdot 10^3$ V/m, the maximum E-field at 10 GHz would then be enhanced by a factor of 1.78 compared to current setup. In Fig. 3.10b, we plotted for reference the square root scaling of the electric field extrema (i.e., at 10 and 18 GHz) with respect to the excitation power.

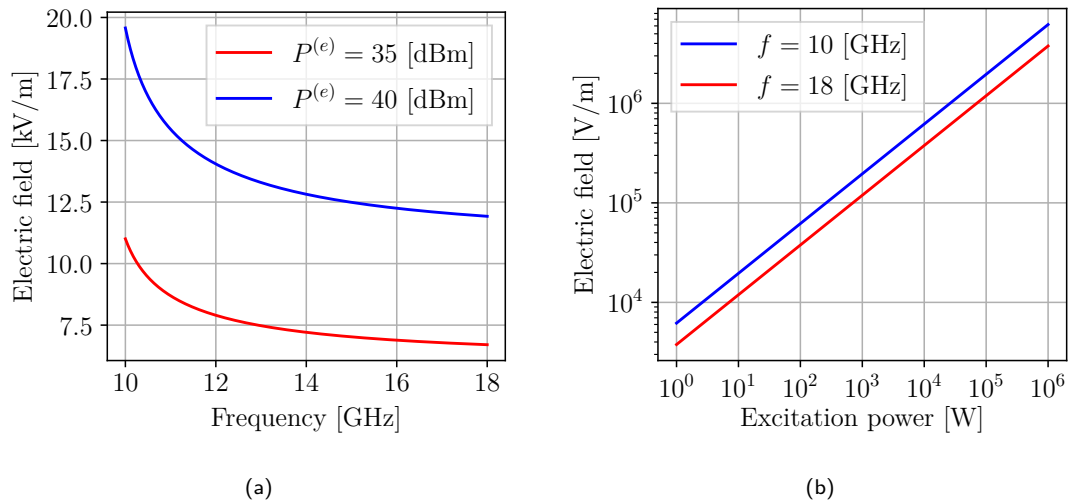


Fig. 3.10. In panel (a), the electric field of the TE_{10} mode inside the waveguide is plotted for an excitation power $P^{(e)}$ of 35 and 40 dBm. In panel (b), we show the square root scaling of the electric field at 10 and 18 GHz with respect to the excitation power.

3.3 Detection module

Before diving into the details of the molecular signals detection, we must first analyse the two protective elements located at the front end of the detection module, namely the single pole double throw (SPDT) switch S2 and the PIN diode limiter D1. Those two devices play an important role during the excitation sequence, where the S2 switch is open (i.e., in its off state) to prevent the 3 W (35 dBm) excitation pulse to damage the following components of the detection chain. In this configuration, the S2 switch has to redirect and absorb the 3 W excitation pulse into a $50\ \Omega$ load. The heat created in this process could potentially damage the switch, which is why the PIN diode limiter is placed at the switch input. Indeed, this component limits the peak power of the signal entering the detection module to 0.1 W (20 dBm), which thus reduces the dissipated power within the switch by a factor of 30. It is worth noting that the PIN diode limiter is linear when the signal power is far below 20 [dBm], a condition that definitely holds for the weak molecular FID signal we are aiming to measure. No distortions are therefore expected to be introduced by this component during the detection sequence.

At the start of that sequence, the S2 switch is closed and the FID signal goes through the first two protective elements, before being amplified by the amplifiers A3 and A4, with a combined gain of 56 dB. The FID signal is then downconverted back to the intermediate frequencies (i.e., between 50 and 250 MHz) through the mixer M2. The down-converted FID signal is then low pass filtered by LPF1, with a cutoff frequency of 250 MHz, discarding any spectral content that would not be related to molecular signal (or at least, not the ones we are interested in). Also, the 250 MHz upper bound for the intermediate frequencies has not been chosen by chance, as it corresponds to half the sampling frequency of the digitizer we are using to digitize the FID signal, namely the Nyquist frequency. Therefore, LPF1 is not only removing the spectral features above this upper bound, but more importantly, it removes the alias of those features that would potentially appear on the digitized spectrum. Before that last step, the FID signal is amplified one last time by the amplifier A5.

In the excitation module, the purpose of the amplifier stages was justified as a mean to obtain the strongest polarization of the molecular sample and thus the strongest electromagnetic molecular response, but what are the motivations for A3, A4, A5 in the detection chain? The goal here, is to maximize the dynamic range of the digitized signal. The dynamic range is defined as the ratio of the maximum value of the signal with the minimum possible value of the digitized signal. Since the minimum possible value is fixed by the digitizer (i.e., by the bit resolution and the vertical range), the dynamic range is then maximised when the maximum value of the signal is equal to the maximum value of the digitizer vertical range. This equality can be achieved with a specific total gain sets by the amplifier stages of the detection module. In practice, the FID signal is so small that we are not able to cover the full vertical range of the digitizer.

3.4 Timing & synchronisation

In order to increase the signal to noise ratio (SNR) of the measured FID, this signal is usually averaged over a large number of shots ($\sim 10^6$). This is only possible if all the presented components are well synchronized and in phase. All the time sequences are defined by the digital delay generator (DDG) and its three outputs T1, T2 and T3. Those outputs generate TTL signals¹ that are represented in Fig. 3.11. This timing diagram describes one excitation-detection or chirp-FID cycle of duration T_{cf} , which is defined by the time that separates two consecutive T1 pulses. The repetition rate of this chirp-FID cycle is thus given by $f_r = 1/T_{cf}$.

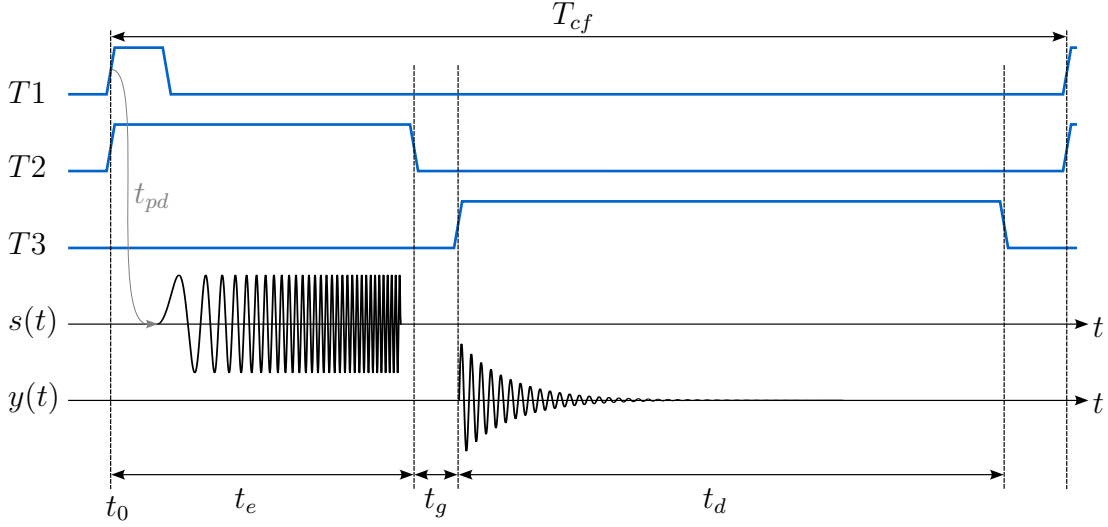


Fig. 3.11. Timing diagram for one chirp-FID cycle of duration T_{cf} . The blue traces are TTL signals where T1 triggers the DDS, T2 controls the excitation switch S1 and T3 controls the detection switch S2. The black traces are time-domain signals where $s(t)$ is the chirped-pulse at the output of the DDS and $y(t)$ is the molecular FID signal at the input of digitizer.

The cycle starts at t_0 on the rising edge of T1 and T2. T1 triggers the DDS that outputs the excitation chirp $s(t)$, after a propagation delay t_{pd} . During this excitation sequence of duration t_e , T2 sends a logic 1 to the excitation switch S1 (as previously shown in Fig. 3.1), allowing the chirp to enter the waveguide static cell and to polarize the molecular sample. After this sequence, T2 sends a logic 0 to the excitation switch S1 which subsequently opens. The excitation and detection sequences are separated by a time gap t_g (i.e., between the opening of S1 and the closing of S2). This is a safety measure to ensure that no high RF power remaining from the excitation chirp will enter the detection module and damage its sensitive components.

After t_g , the detection sequence begins when T3 sends a logic high signal to the S2 switch, which then closes for a duration t_d . It thus allows the FID signal $y(t)$ to enter the detection module and to eventually be measured by the digitizer. The remaining time $T_{cf} - t_e - t_g - t_d$ of the cycle is unused and serves only as padding

¹Transistor-transistor logic signals set to either 0 or 5 [V] DC voltage to represent a logic 0 or logic 1, respectively

between successive chirp-FID cycles. A typical timing sequence used throughout this project is displayed in Table. 3.1

Table 3.1: Typical chirp-FID timing sequence.

T_{cf} [μs]	t_e [μs]	t_g [μs]	t_d [μs]	t_{pd} [μs]
20	1.5	0.15	5	< 0.1

If one wants to perform a large number of those chirp-FID cycles where $y(t)$ is digitized on each cycle with the same phase (with respect to the sample points), then the DDG alone is not sufficient to synchronise the experiment. Indeed, if the DDG controls the precise time at which it triggers the DDS, it has no control over the time at which it is registered by the DDS, which should happen on the rising edge of its clock.

Over multiple chirp-FID cycles, the DDS receives a trigger t_0 defined on the rising edge of the DDG internal clock CLK_{DDG} , taken as the time reference for this example, illustrated in Fig. 3.12. The trigger is registered on the rising edge of the DDS clock CLK_{DDS} , indicated by the red dots on the illustration. If the phase of CLK_{DDS} fluctuates randomly with respect to CLK_{DDG} , then the red dots will be distributed randomly between t_0 and $t_0 + T_{C,DDS}$, over the course of multiple chirp-FID cycles (with $T_{C,DDS}$, the clock cycle duration of the DDS). This phenomenon is known as jitter.

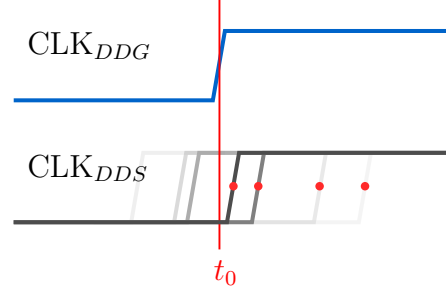


Fig. 3.12. Jitter illustration.

This means that the propagation delay t_{pd} will also vary randomly such that the phase of the chirp and thus the phase of the FID, will not be reproducible between successive acquisitions. Here we took an example for the DDS, but jitter will also occur for any component that runs with its own clock such as the digitizer and the local oscillator G2.

To circumvent this problem, the clocks of the DDG, DDS, G1, G2 and the digitizer need to be in phase. The synchronization is achieved by the GPS disciplined oscillator (GPSDO), that generates a 10 MHz reference signal, which is then distributed to those 5 components. The 10 MHz signal is then multiplied according to the clock specification of each component.

3.5 RF chains analysis

The detailed analysis of both RF chains is provided in the section. The figures of merit of the excitation chain are displayed in Table 3.2. For each component, the

bandwidth BW , the insertion IL and the gain G are provided. The last column of this table gives the power available at the output of each component, using the DDS output as a starting point. The DDS output is approximatively 0 dBm (measured value) but a 3dB splitter was used in practice to monitor the pulse during the experiments, which is not represented in Fig. 3.1. The power output of the DDS is adapted accordingly in Table. 3.2. Based on these figures, the power available at the input port of the waveguide static cell is estimated to be 33.4 dBm.

Table 3.2: Excitation chain.

Component	BW [GHz]	IL [dB]	G [dB]	P_{out} [dBm]
DDS	$DC - 1$	-	-	-3
M1	$7.5 - 20$	7	-	-10
A1	$6 - 18$	0	28	18
Att1	$DC - 18$	18	-	0
A2	$5.9 - 18$	0	35	35
S1	$DC - 20$	1.6	-	33.4

The same analysis is performed for the detection chain in Table. 3.3, but the last column is now dedicated to the noise figure NF of each component. The cumulated gain of the detection RF chain is 55.9 dB. This large cumulated gain is required to observe the very weak FID signal emitted by the molecules.

Table 3.3: Detection chain.

Component	BW [GHz]	IL [dB]	G [dB]	NF dB]
D1	$2 - 18$	1.8	-	1.8
S2	$DC - 20$	1.6	-	1.6
A3	$6 - 18$	0	28	5.5
A4	$6 - 18$	0	28	5.5
M2	$7.5 - 20$	7	-	7
LPF1	$DC - 0.25$	1.7	0	1.7
A5	$0.3 - 14$	0	12	5.5

The total noise figure of the detection chain is computed with the Friis formula for noise: [31]

$$F_{tot} = F_1 + \frac{F_2 - 1}{G_2} + \frac{F_3 - 1}{G_1 G_2} + \frac{F_4 - 1}{G_1 G_2 G_3} + \dots + \frac{F_n - 1}{G_1 G_{2n-1}} \quad (3.9)$$

where F_i is the noise factor of the i -th component of the detection chain, following the direction of the signal path. The noise factor is simply the linear form of the noise figure and is therefore given by:

$$F = 10^{NF/10} \quad (3.10)$$

The gain G_i of the i -th component is also expressed in linear scale. The total noise factor is thus evaluated as:

$$F_{tot} = 1.51 + 0.64 + 5.6 + 8 \cdot 10^{-3} + \dots = 7.76 \quad (3.11)$$

which therefore gives a total noise figure of $NF_{tot} = 8.9$ [dB]. The equation 3.11 is expanded to show the major contribution of the third term to the total noise factor, due to both attenuation gains in the denominator G_1G_2 . Having the PIN diode limiter D1 followed by the detection switch S2 at the input of the detection chain increases considerably the noise figure. Furthermore, the noise figure of the first amplifying stage (i.e. A3) has no impact at all on the NF_{tot} . The fact that the amplifier A3 is not a low noise amplifier (LNA) has thus little consequences. Ideally, the PIN diode limiter would have to be removed to take advantage of an LNA.

Chapter 4

First results and improvements of the CP-FTMW spectrometer

Now that the working principle and general design of the CP-FTMW spectrometer are introduced, this chapter is dedicated to the results that contributed to validate and improve the instrument. The collection of those results has been an iterative process. First, we established the experimental setup capable to detect a first molecular signal. Then, we used that molecular signal as a benchmark to assess the improvements resulting from some key modifications. Those results and key modifications are presented in that order.

4.1 First spectra

Once the spectrometer is operational, a molecular species must be introduced into the waveguide static cell and probed by the instrument. The considered molecules have to meet certain criteria. First, as stated in the previous chapter, it is mandatory that the molecule of interest displays known transitions within the TE_{10} frequency bandwidth of the waveguide, as the excitation and molecular signals would simply not propagate otherwise. Moreover, since the spectrometer is yet to be optimized, the aimed transition must have a large transition dipole moment which radiates a molecular signal sufficiently strong, and therefore reduces the sensitivity requirement of the non-optimized instrument. In the Cologne Database for Molecular Spectroscopy (CDMS), it is shown that methanol (CH_3OH), possesses one of its strongest transitions located at 12178.6 MHz, which makes it a molecule of choice to test the instrument. The methanol line list of the CDMS catalogue is accessible in Ref. [33] and the calculation of the quantum numbers is given in Ref. [34].

As developed in the previous chapter, the DDS produces excitation signals in the 50-250 MHz frequency range and thus needs to be up-converted. To this end, the LO signal produced by the synthesizer G2 is set to 12100 MHz to excite and detect the methanol transition at 78.6 MHz, in the intermediate frequencies. Then, the DDS is programmed to send a chirp whose frequency is linearly swept from 50 MHz to 80 MHz, in 1 μs which is assumed to be a pulse time short compared to

the T_2 relaxation time. The transition is polarized at the end of the chirp to detect the transient emission rapidly after it was excited.

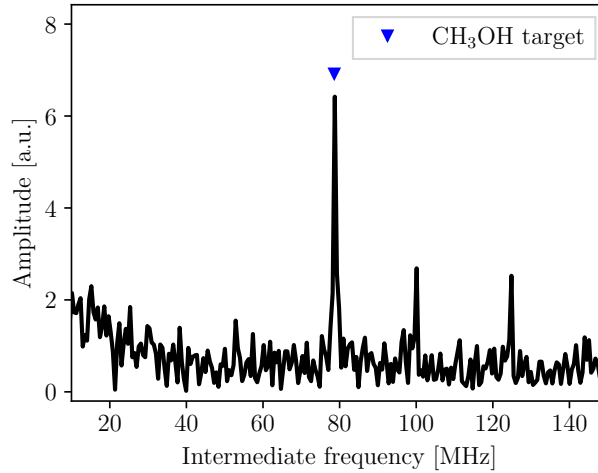


Fig. 4.1. First spectrum performed with CH_3OH , $p = 20$ [mbar]

In those conditions, 8192 phase-stable FIDs are acquired on the digitizer and co-added to reduce the background noise. After taking the Fourier transform of the averaged FID signal, the molecular spectrum in Fig. 4.1 is finally obtained, where a spectral line is observed at the intermediate frequency of 78.6 MHz. The line peak is 6 times larger than the noise floor of the spectrum. The intensity of the transition line with respect to the noise floor of the spectrum is defined as the amplitude-signal-to-noise ratio (aSNR). The aSNR for this instance is thus 6. Minor peaks are also observed around the transition and are not associated with any molecular transitions. These peaks are the result of internal signals of the spectrometer electronics (e.g., clock signals) which are leaked in the detection signal path. In the remaining of this thesis, those signals are referred to as spurs and are differentiated from molecular signal by labelling the transition with a blue inverted triangle, as illustrated in the figure above.

This first signal was acquired with a less optimized spectrometer setup than the one presented in the previous chapter. At the time of this first acquisition, the excitation switch S1 was placed before the preamplifier of the excitation chain, as illustrated in case (b) of Fig. 4.2. The impact of the excitation switch placement in the excitation chain on the sensitivity of the instrument has been evaluated by testing the three configurations displayed in Fig. 4.2.

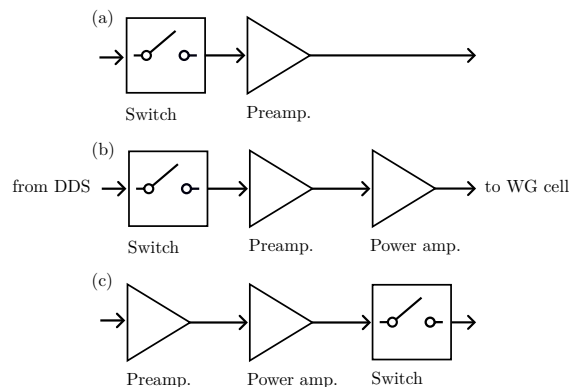


Fig. 4.2. Blanking switch

For the configuration (a), the power amplifier is removed from the excitation chain to compare the resulting noise level with the configuration (b). The resulting spectra are shown in the left panel of Fig. 4.2. The aSNR is similar for both

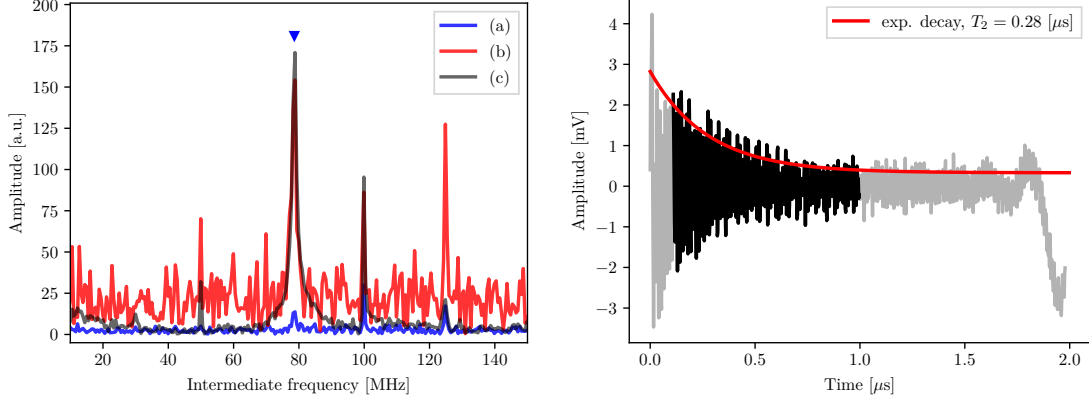


Fig. 4.3. The left panel displays the spectra acquired with the three configurations (a), (b) and (c) presented in Fig. 4.2. The right panel shows the time domain molecular FID signal acquired with the configuration (c) of the excitation module. The bold part of the trace highlights the set of data points that were used to fit the exponential decay of the FID, depicted on the red trace, with an estimated relaxation time $T_2 = 0.28 \text{ } [\mu\text{s}]$.

configurations, but the noise level obtained in case (b) is about 8 times larger than the one of case (a). This means that during the detection sequence, when no chirped pulse is broadcast in the waveguide static cell, the noise emitted by the power amplifier dominates any noise produced in the detection module. It is stated in the literature that the power amplifier used in a CP-FTMW spectrometer must include a blanking noise control if one wants to detect the molecular emission without the background noise of the amplifier. [23] However, this type of amplifiers are expensive and difficult to find. It is possible to circumvent this technological challenge by outsourcing the blanking noise control to a switch placed at the output of the power amplifier. [35] This second alternative justified the implementation of the configuration (c), where the excitation switch S1 is placed at the output of the power amplifier.

The spectrum obtained in this last case is overlaid to the spectra obtained with the two first configurations in the left panel of Fig. 4.2. The spectrum (c) displays a similar line intensity as the one obtained in the configuration (b) and has a noise floor comparable to the one observed in the (a). Therefore, it is concluded that placing a blanking switch at the output of the power amplifier improves the sensitivity of the spectrometer by a factor of 8, which gives in this case an $\text{aSNR} \sim 50$. This significant gain in sensitivity gives the opportunity to observe the decaying molecular FID in the time domain, shown in the right panel of Fig. 4.2. The black section of the signal represents the part of the FID that is used to evaluate the relaxation time constant T_2 . Only the local maxima of this time interval are kept. The resulting set of points is then fitted with an exponential of the form:

$$y(t) = ae^{b(x-c)} + d \quad (4.1)$$

The fitting curve $y(t)$ is traced in red on the FID signal of Fig. 4.3 and the relaxation time constant is estimated by $T_2 = -1/b = 0.28 \text{ } [\mu\text{s}]$.

4.2 Digitizer & Data acquisition

Another key aspect of the instrument is the speed at which its digitizer is able to acquire the successive molecular emission signals. Since the sensitivity of the instrument improves with the square root of the number of co-added FIDs, doubling the number of molecular acquisitions in a given time frame improves the aSNR by a factor of $\sqrt{2}$. The spectra presented so far were all recorded using an oscilloscope Agilent Technologies DSO7104A (DSO). For instance, the spectra on the left panel of Fig. 4.2 were computed based on 32k molecular FID signals, averaged together to give the resulting FID signal on the right panel of the same figure. Each of those 3 experiments took approximatively 10 minutes to complete, with a data acquisition (DAQ) rate of ~ 53 Hz. This DAQ rate is far inferior to the ones reported in the literature, where DAQ rates obtained with similar DDS-based CP-FTMW instruments are on the magnitude of several kilohertz. [3, 5]

The bottleneck induced by the averaging speed led to the replacement of the DSO oscilloscope by an USB oscilloscope TiePie HS5-540XM (HS5), whose key characteristics are compared with the former digitizer in Table 4.1. The strength of the HS5 digitizer lies in its very large memory (i.e., 8 times bigger than the DSO oscilloscope). When one FID signal per shot is acquired (as done previously), the oscilloscope has to re-arm and trigger between each cycle, which implies an overhead time at the beginning of each acquisition. [5] But if multiple FIDs are acquired in one single shot (i.e., the digitizer is triggered once and samples multiple FID signals without interruption), then the overhead duration becomes negligible compared to the acquisition and transfer times. Therefore, a digitizer capable of acquiring a large number of FIDs in its memory minimizes the impact of the overhead time prior to each acquisition.

Table 4.1: Digitizers comparison.

Digitizer	Sampling frequency [GHz]	Memory [MSa]	Resolution [bit]	Price [€]
Agilent	4	8	8	> 10k
HS5	0.5	64	12	~ 1 k

The new averaging scheme to increase the DAQ rate of the spectrometer is illustrated in Fig. 4.4 and is developed in this paragraph. The HS5 digitizer runs in a “block mode” where a block B_i is a single large acquisition which contains n chirp-FID cycles denoted $C_{i,j}$. Once the block measurement is collected in the memory of the digitizer, the block is immediately transferred to the computer via USB which stores this block in a 32-bit C buffer. During this experiment, m blocks are collected in total by the digitizer and accumulated in the C buffer of the computer. At the end of the experiment, the C buffer contains the accumulated blocks $\sum_{i=1}^m B_i$. This C buffer is finally split in n segments where the j -th segment is $\sum_i^m C_{i,j}$, co-added and divided by $(m \times n)$ to give the final result:

$$\tilde{C} = \frac{1}{mn} \sum_i^m \sum_j^n C_{i,j} \quad (4.2)$$

where $\tilde{C}$ is the chirp-FID cycle resulting from the averaging of $(m \times n)$ chirp-FID cycles.

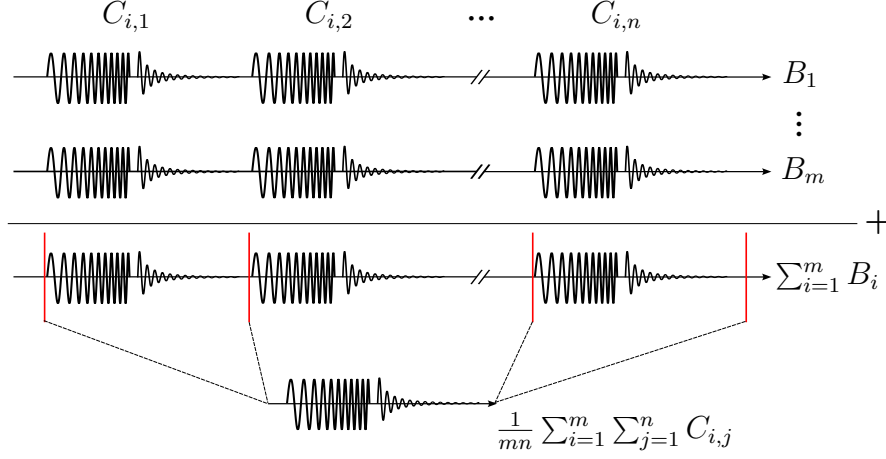


Fig. 4.4. Illustration of the averaging scheme performed by the DAQ C program. The red vertical lines indicate the cuts performed in the sequences.

A practical example of this averaging scheme is developed in this paragraph where a 10^6 averages experiment is performed. First, the size of each measurement block is set to 50 MSa and are populated at a sampling frequency of 500 MSa/s. A single block is thus acquired in 100 ms. To fix the number of chirp-FID cycles per block, the repetition rate is set to $f_r = 50$ [kHz] on the DDG. Each block thus contains 5000 chirp-FID cycles of $20 \mu\text{s}$. Finally, the digitizer is programmed to acquire 200 measurements blocks, which makes in total 10^6 acquired FIDs. After the experiment, the C buffer of the computer which now contains the 200 accumulated blocks is processed following Eq. 4.2 and the C program returns the resulting chirp-FID signal displayed in Fig. 4.5, averaged 10^6 times, after a total elapsed time

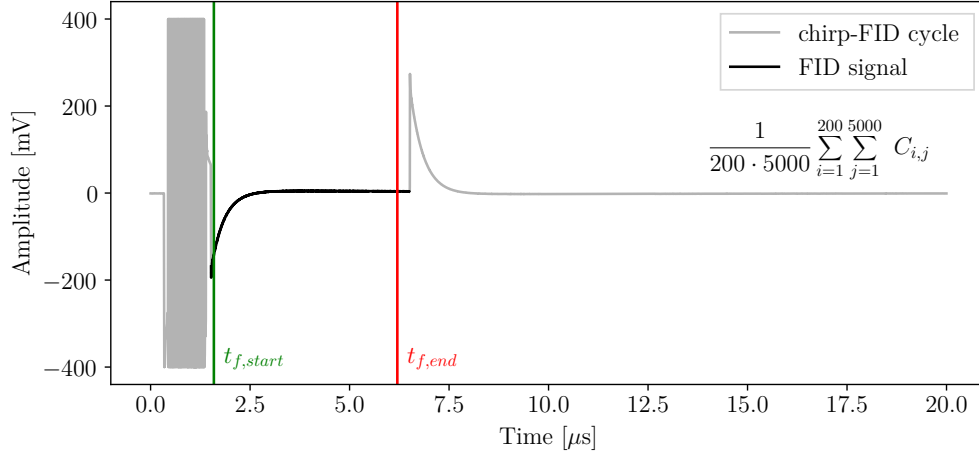


Fig. 4.5. Time domain signal of the chirp-FID cycle of duration $T_{cf} = 20 \mu\text{s}$ and averaged 10^6 times, with $m = 200$ and $n = 5000$. The bold black segment corresponds to the detection interval t_d , where the molecular signal is captured. The green and red vertical lines enclose the analysis window $[t_{f,start}, t_{f,stop}]$ where the molecular FID is studied, the signal outside of this interval is discarded.

of 9 minutes. With a data acquisition rate of ~ 1.9 kHz, this technique is thus 35 times faster than the previous method. This gain in data acquisition speed allows to acquire 1 million molecular FID signals in less time than what was previously

required to reach 32k averages.

It is worth noting that since the digitizer acquires multiple chirp-FID cycles per acquisition, the averaging is performed on the full $20\ \mu\text{s}$ chirp-FID signal. It is by no means a limitation since it provides the freedom to define afterwards the precise time frame $[t_{f,start}, t_{f,stop}]$ required for analysis and post-processing. Another legitimate concern that one may have is the presence of the chirp in the signal depicted in Fig. 4.5. Indeed, according to the timing diagram of Fig. 3.11, the detection switch S2 is open during the excitation interval t_e and the chirp is thus blocked by the switch at the input of the detection module. In practice, the chirp is so intense that a fraction of its power is transmitted through the switch and is therefore visible on the averaged chirp-FID signal.

In Fig. 4.6, the elapsed time as a function of the number of averages is displayed. The red trace indicates the theoretical elapsed time with no overhead time t_{oh} and is thus only limited by the transfer time of the USB2.0 and the measurement time set by the repetition rate of the experiment. As announced previously, the acquisition time t_{acq} approaches this theoretical limit as the number of FIDs per acquisition increases. Once the number of averages exceeds 10^4 (i.e. the maximum number of FIDs per block), then multiple blocks are necessary to complete the experiment and the difference between the acquisition time t_{acq} and the theoretical limit remains constant.

The blue trace corresponds the 100% duty cycle limit, that is an acquisition time of $t_{acq} - t_{oh} - t_{tr}$ only limited by the duration of the measurements. The gap between the 100% duty cycle limit and the red limit is set by the transfer rate of the USB2.0 transfer protocol of the digitizer. This result shows that the large memory of the HS5 digitizer only converges towards the red limit imposed by the USB2.0 transfer rate and that a digitizer with a better transfer protocol is thus required to improve further the duty cycle of the experiment.

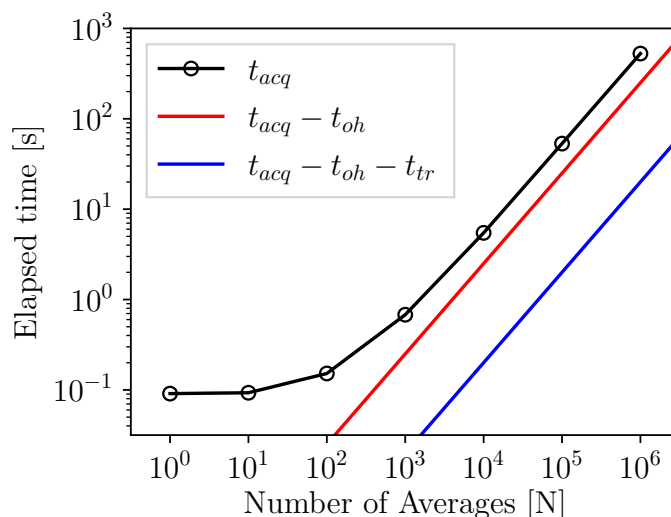


Fig. 4.6. DAQ time as a function of the number of averages. The red trace the theoretical limit with no overhead time and the blue trace is theoretical limit with no overhead and transfer times.

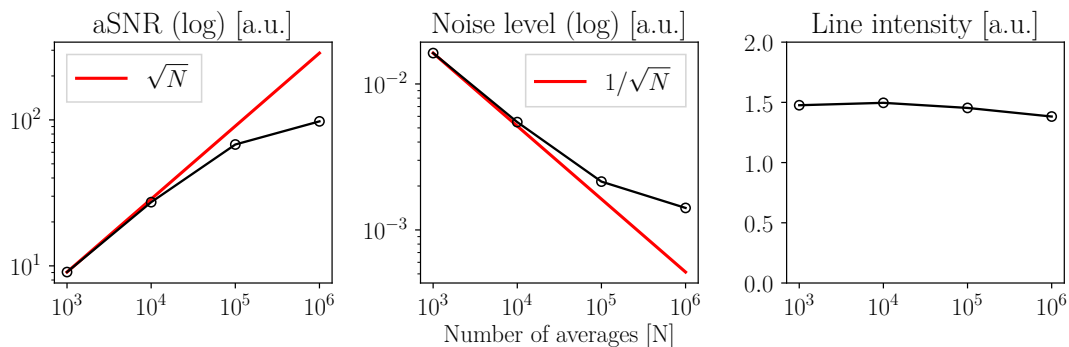


Fig. 4.7. The aSNR (left panel), the noise floor (middle panel) and the line intensity (right panel) are plotted with respect to number of averages N .

With the ability to perform a large number of averages, it is now possible to evaluate the square root scaling of the aSNR with respect to the number of averages, as shown in the left panel of Fig. 4.7. The aSNR deviates from the square root scaling due to the deterioration of the noise. As presented in the next section, parasitic peaks in the noise floor of the spectra increase with the number of averages. The line intensity of the methanol is mostly stable with the increase of averages, showing that the spectrometer is phase-stable during the experiments.

4.3 Post-processing

The treatment of the acquired molecular signals is the last stage required to obtain the actual spectra. During the characterization stage of this work, the benchmark methanol transition is rather easy to locate in the 50-250 MHz intermediate frequency band. In future applications, the instrument will have to perform broadband (several gigahertz) detection of unknown molecules. In these conditions, labelling the transitions happens to be very challenging if the spectra are corrupted by spurious features. To remove those spurs, it is therefore important to implement efficient filtering and background subtraction techniques.

4.3.1 Infinite impulse response filtering

The 20 μ s chirp-FID signal presented in Fig. 4.5 is the result of an experiment performed with a 50 kHz repetition rate and 10^6 averages. Directly after the chirp, the black outlined part of the trace corresponds to the detection sequence which contains the molecular FID signal. At the start of the detection sequence, the detection switch S2 is closed and generates an intense low frequency transient response, superimposed to the FID signal, as shown in Fig. 4.8.

To study the molecular FID signal, the chirp-FID signal is cropped slightly after (before) the switching edges at $t_{f,start}$ ($t_{f,stop}$), which define the analysis window shown in Fig. 4.8. Then, to retrieve the centered FID signal, the intense low frequency (LF) component is extracted with a low pass infinite impulse response (IIR) filter, depicted on the red trace of Fig. 4.8, and subtracted from the raw FID

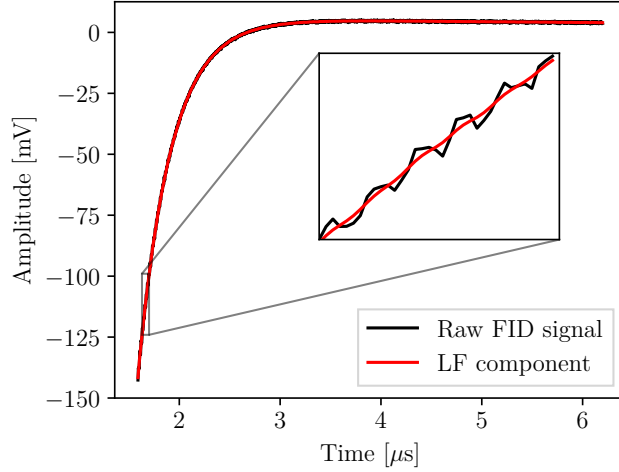


Fig. 4.8. Analysis window of the chirp-FID cycle defined by $t_{f,start} = 1.5$ and $t_{f,stop} = 6.5 \mu s$, centered on the raw FID signal (black trace). The intense low frequency component of the FID signal is isolated on the red trace.

signal, depicted on the black trace of the same figure. The IIR filter chosen for this task is the Butterworth filter of order 1, with a cutoff frequency of 5 MHz.

The Fourier transform of both raw and LF subtracted FID signals is displayed in Fig. 4.9. One can observe that all the spectral elements of the LF subtracted spectrum are dominated by the raw spectrum, which therefore hides the true noise floor of the FID spectrum. Also, the methanol transition line shape is not only scaled down but is also distorted by the LF component. The subtraction of the LF component is thus mandatory to reveal the transition lines of the spectrum.

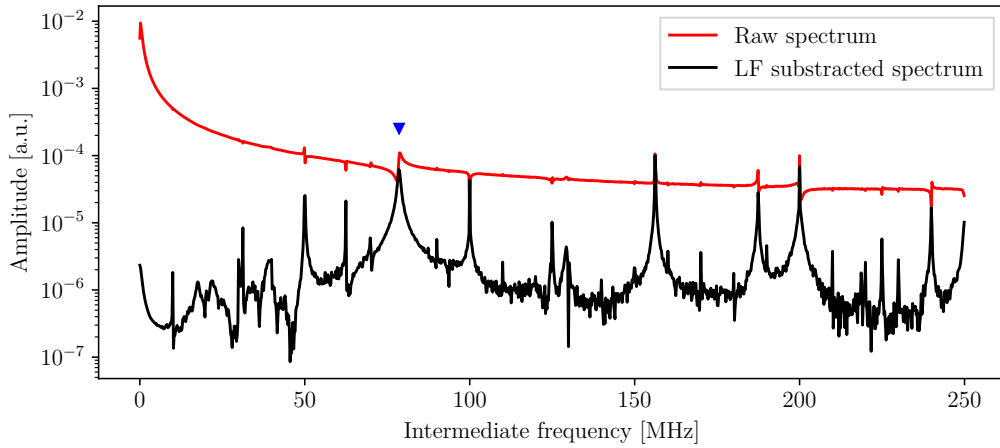


Fig. 4.9. The Fourier transform of both the raw FID signal that includes a large low frequency component (red trace) and the raw FID signal subtracted by the low frequency component (black trace). The traces are plotted on a log y -scale.

4.3.2 Pattern filtering

In Fig. 4.10, one can observe the time domain FID signal resulting from the IIR filtering of the original signal, previously shown in Fig. 4.8. With its characteristic exponentially decaying envelope, the molecular FID signal falls very rapidly into the noise, around $2.5 \mu\text{s}$ in this case. Furthermore, the noise that remains in the signal is mostly periodic, as hinted by the many sharp spurious features of the corresponding spectrum in Fig. 4.9.

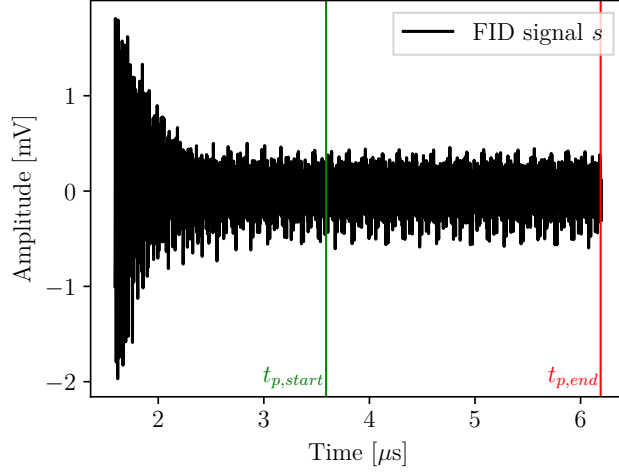


Fig. 4.10. Molecular FID signal s after IIR filtering. The interval $[t_{p,start}, t_{p,end}]$ captures the periodic noise superimposed to the signal.

After investigation, it has been found that most of the spurs are actually introduced by the HS5 digitizer, which is not only leaking the 10 MHz external clock signal, but also the trigger signal coming from the DDS. The periodic noise produced by those leaked signals is not *stricto sensu* periodic, but rather is the sum of a few periodic patterns $P_k(t)$ that can be expanded as Fourier series and are expressed as:

$$P_k(t) = a_{0,k} + \sum_{n=1}^{+\infty} a_{n,k} \cos(2\pi n f_{0,k} t) - \sum_{n=1}^{+\infty} b_{n,k} \sin(2\pi n f_{0,k} t) \quad (4.3)$$

where each pattern $P_k(t)$ has a fundamental frequency of $f_{0,k}$. [36] In the case of the FID signal from Fig. 4.10, it is expected to find two patterns in the periodic noise, associated to both leaked signals described earlier. To remove those patterns, the pattern filter proposed by Brian Hays in Ref. [37] is implemented. For this instance, the pattern filter algorithm reads as follows:

1. First, an interval $[t_{p,start}, t_{p,end}]$ is chosen in the FID signal where the actual FID has vanished and is mostly periodic noise, as shown in Fig. 4.10. this interval is denoted by n_p , namely the time series of size $M = 1300$ samples, which holds the periodic noise information.
2. The fundamental frequency of the first dominant pattern (which is a priori unknown) is retrieved with the correlation between n_p and a truncated version

of itself denoted $\tilde{n}_p$, with a size $L = 200$ (i.e., the first 200 samples of n_p). The correlation is expressed as:

$$c[k] = \sum_{m=0}^{L-1} n_p[m+k] \cdot \tilde{n}_p[m] \quad (4.4)$$

where the integer k is the sample lag. To ensure the overlap between the two sequences, the correlation $c[k]$ is evaluated on $k = 1, 2, \dots, M - L + 1$, as shown in Fig. 4.11.

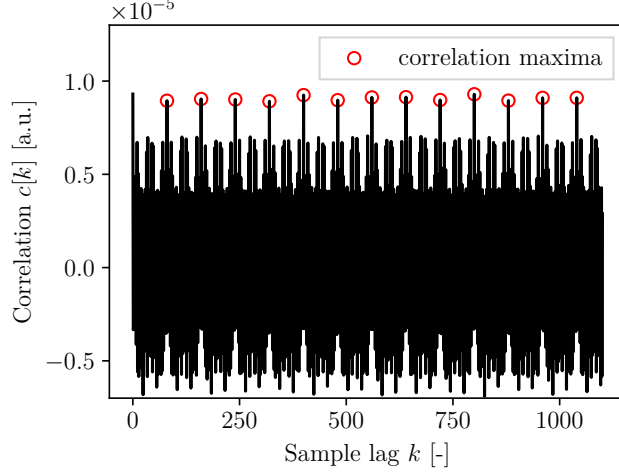


Fig. 4.11. Correlation function of n_p with $\tilde{n}_p$. The maxima (red circles) are periodic with a period of 80 samples.

The correlation shown in that figure displays periodic maxima (red circles) with an amplitude similar to $c[0]$ and are repeated every 80 samples. Since the sampling frequency of the HS5 digitizer is set to 500 MHz, it gives a repetition frequency of 6.25 MHz. We thus resolved the fundamental frequency of the first dominant pattern $P_1(t)$ present in the FID signal, with $f_{0,1} = 6.25$ [MHz], $T_{0,1} = 1/f_{0,1} = 0.16$ [μ s] and a pattern length of $L_{p,1} = 80$ samples.

3. Once the fundamental frequency of the pattern is recovered, a one period estimation $\hat{P}_1[n]$ of length $L_{p,1} = 80$ is constructed by slicing the n_p sequence into $\lfloor M/L_{p,1} \rfloor = \lfloor 1300/80 \rfloor = \lfloor 16.25 \rfloor = 16$ sub-sequences and discard the remaining samples. Those sub-sequences are then averaged together to finally give the one period pattern estimation $\hat{P}_1[n]$, written as:

$$\hat{P}_1[n] = \sum_{m=0}^{\lfloor M/L_{p,1} \rfloor - 1} n_p[n + mL_{p,1}] \quad (4.5)$$

4. Then, as shown in Fig. 4.12a, the one period pattern estimation is propagated to cover the full molecular FID sequence. The inset of the same figure allows to visually check the fit quality between the periodic noise and the pattern estimation $\hat{P}_1$. It can also be verified in Fig. 4.12b that the harmonics of $\hat{P}_1$ in the frequency domain are actually matching the spurs of the FID spectrum. In this case, the harmonics of $\hat{P}_1$ cover all the major spurs in the spectrum confirming that P_1 is indeed the major pattern that contributes to the periodic noise.

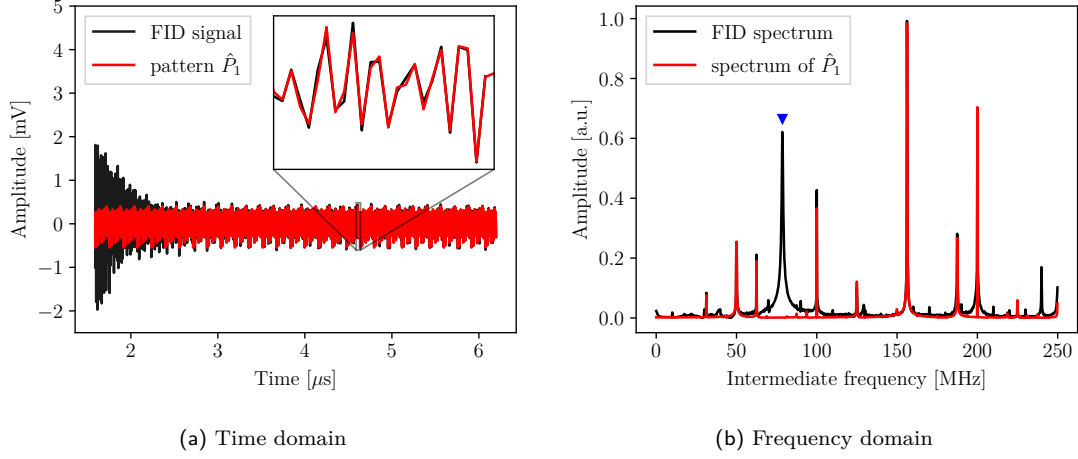


Fig. 4.12. In the left panel (a), the estimated pattern $\hat{P}_1$ is superimposed to the FID signal. The inset magnifies a section of the periodic noise that is fitted by $\hat{P}_1$. The right panel (b) shows the FID spectrum (black trace) and the Fourier transform of $\hat{P}_1$ (red trace).

5. Finally, the estimated pattern $\hat{P}_1$ is simply subtracted from the FID signal in the time domain to remove the harmonic spurs associated to the fundamental frequency $f_{0,1}$, in the frequency domain. The result of this operation yields the filtered FID signal. The algorithm is then repeated and applied on its output until it is no longer possible to observe periodic maxima in the correlation sequence computed in step 2.

As expected, for this particular FID signal, only 2 passes with the pattern filter are required to remove a first pattern P_1 with $f_{0,1} = 6.25$ MHz, as thoroughly demonstrated in the algorithm above, and a second pattern P_2 with $f_{0,2} = 10$ MHz. Since the 10 MHz external clock signal is trivially identified to P_2 it is concluded that P_1 originates from the DDS trigger. Furthermore, it is specified in the DDS datasheet that the AD9915 chip is internally clocked by a 156.25 MHz signal, which happens to be the strongest spur in the FID spectrum, as shown in Fig. 4.12b. The FID signals and spectra that result from the pattern filter iterative algorithm are displayed in Fig. 4.13.

In Fig. 4.13a, a large reduction in periodic noise is observed for both filtered signals compared to the unfiltered FID signal. Most of this noise reduction occurs in the first pass of the pattern filter demonstrating that P_1 is indeed larger than P_2 . The same observation is made in the frequency domain (Fig. 4.13b) where most of the dominant spurs are removed with the filtering of P_1 , leaving only a few small spurs (on the blue trace) to be removed with the filtering of P_2 .

Even though most of the spurious features have been removed, some broad spectral lines still remain in the final filtered spectrum. This observation highlights the main weakness of the pattern filter, namely the inability to detect and remove transient noise that are localized in the time domain and thus broadened in the frequency domain. Upon verification, it happens that high frequencies transient signals (around 100 MHz and 200 MHz) are buried below the FID, at the beginning of the time domain sequence. This transient signal may be introduced by the RF components when the detection switch S2 closes. As the transient noises cannot

be treated by the pattern filter, a third and last stage is required in the signal processing pipeline, presented in the next section.

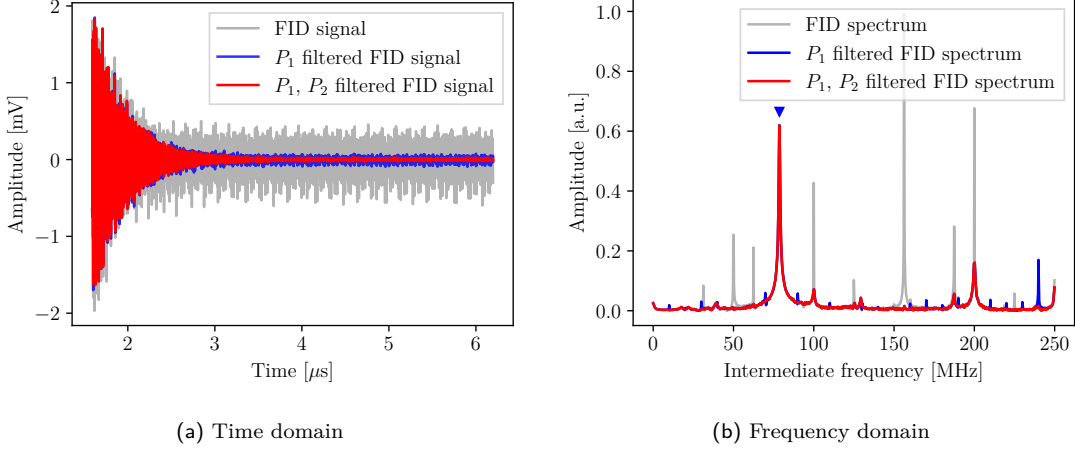


Fig. 4.13. The left panel (a) displays the filtered FID signals obtained after one and two stages of pattern filtering (on the blue and red traces, respectively) compared to the base FID signal (gray trace). The right panel (b) displays the respective FID spectra.

4.3.3 Background subtraction

Background subtraction allows to remove broad spurs that are caused by non-periodic (i.e., transient) noise in the time domain. In addition to the FID spectrum acquisition which have been acquired, this technique requires a second experiment performed with the exact same experimental settings, except for the absence of molecular sample in the waveguide static cell. With no molecular transitions to detect, the spectrum that results from this experiment is called the background spectrum. As shown in Fig. 4.14, the background spectrum (black trace) and the FID spectrum (red trace) ideally contains the same spurious content. Note that both spectra have gone through the exact same IIR and PF stages.

One could naively think that the subtraction between both spectra would suffice to get rid of the parasitic spectral lines. Unfortunately, both FID and background discrete spectra, that are respectively denoted $F[n]$ and $B[n]$, potentially take complex values for which magnitude alone does not allow for such subtraction, i.e., both magnitude and phase should be equated between the spectra. It has been found that a phase shift $\Delta\phi(\omega)$ exists between both spectra which is neither constant, nor linear with respect to the frequency, the latter being the expected result in case of a phase shift resulting from a delay in the time domain. As it is not possible to globally compensate the phase shift, a local background subtraction algorithm has been implemented and is described as follows:

1. First, all the peaks in $F[n]$ and $B[n]$ are identified with a *built-in* peak finder function. This function returns two index sets $\{p_{f,i}\}_{i=1,\dots,M}$ and $\{p_{b,j}\}_{j=1,\dots,N}$ that contain the indices of the peaks in the FID and background sequences, respectively.

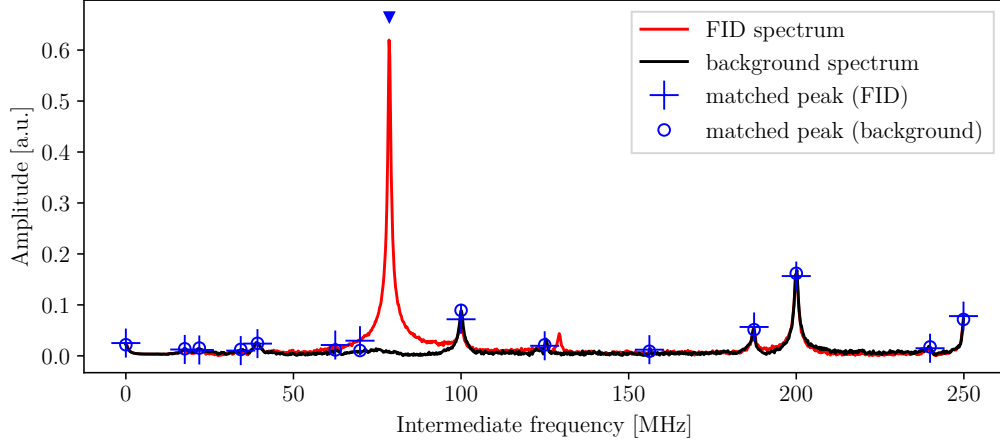


Fig. 4.14. FID (red trace) and background (black trace) spectra, after pattern filtering. Detected peaks that match within 3 spectral samples (~ 430 kHz) between the FID (blue cross) and the background (blue circle) spectra

2. Then, the spurious content are discriminated from the random peaks using the following algorithm:

Algorithm 1 Spur detection in index sets $\{p_{f,i}\}_{i=1,\dots,M}$ and $\{p_{b,j}\}_{j=1,\dots,N}$

```

 $S \leftarrow \{\emptyset\}$ 
 $i \leftarrow 1$ 
 $j \leftarrow 1$ 
for  $i \leq M$  do
  for  $j \leq N$  do
    if  $|p_{f,i} - p_{b,j}| < 3$  then
       $S \leftarrow S \cup \{p_{f,i}\}$ 
    end if
  end for
end for
return  $S$ 

```

This algorithm returns a new index set S that contains the indices of the spurs detected in both $F[n]$ and $B[n]$. We allowed for a 2 samples mismatch (~ 650 kHz) in the spur detection algorithm. Those detected spurs are marked in Fig. 4.14 on the FID (blue cross) and the background (blue circle) spectrum. With those blue markers, one can verify that the spurs have the same magnitude between both spectra (far from the molecular transitions, since the transition magnitude adds up to the spur).

3. For every spurs indexed by $s \in S$, two intervals $F_s[n]$ and $B_s[n]$ of length $L = 9$ are extracted and are centered on s from $F[n]$ and $B[n]$, respectively. A constant phase shift $\phi_s = \angle F_s[n] - \angle B_s[n]$ is assumed and must be corrected to subtract the corresponding spur. To do so, the estimated phase shifts $\hat{\phi}_s$ are evaluated using the least square minimization method:

$$\hat{\phi}_s = \arg \min_{\phi_s} \sum_{n=0}^{L-1} \left(F_s[n] - \tilde{B}_{s,\phi_s}[n] \right)^2 \quad (4.6)$$

Where $\tilde{B}_{s,\phi_s}[n]$ are the rotated spectral coefficients from the background spectrum, obtained upon the rotation:

$$\begin{pmatrix} \text{Re}\{\tilde{B}_{s,\phi_s}[n]\} \\ \text{Im}\{\tilde{B}_{s,\phi_s}[n]\} \end{pmatrix} = \begin{pmatrix} \cos(\phi_s) & \sin(\phi_s) \\ -\sin(\phi_s) & \cos(\phi_s) \end{pmatrix} \begin{pmatrix} \text{Re}\{B_s[n]\} \\ \text{Im}\{B_s[n]\} \end{pmatrix} \quad (4.7)$$

At this stage, the sequences $F_s[n]$ and $\tilde{B}_{s,\hat{\phi}_s}[n]$ should have the same magnitude and the same phase.

4. Finally, the collection of phase-corrected background spurs $\{\tilde{B}_{s,\hat{\phi}_s}[n]\}_{s \in S}$ from the FID spectrum $F[n]$, which gives the new background subtracted FID spectrum $F_{BS}[n]$, defined as:

$$F_{BS}[n] = \begin{cases} F[n] - \tilde{B}_{s,\hat{\phi}_s}[n - s + \frac{(L+1)}{2}] & : s - \frac{L-1}{2} \leq n \leq s + \frac{L-1}{2}, \forall s \in S \\ F[n] & : \text{otherwise} \end{cases}$$

In Fig. 4.15, $|F_{BS}[n]|$ is superimposed to the spectrum that was obtained after the pattern filter. It is observed that the broad spectral lines induced by the transient noise have disappeared as the result of the background subtraction. Around 129 MHz, one can observe a small peak which has not been removed. this result has been reproduced multiple times and this peak does not occur in any of the background spectra. Upon verification in the Cologne Database for Molecular spectroscopy, it happens that the second most intense methanol transition at room temperature is located at 12229.348 MHz, and thus at 129.348 MHz in the intermediate frequencies (since $f_{LO} = 12100$ MHz). It is concluded that this methanol transition is actually the tiny spectral line that is observed in the spectrum.

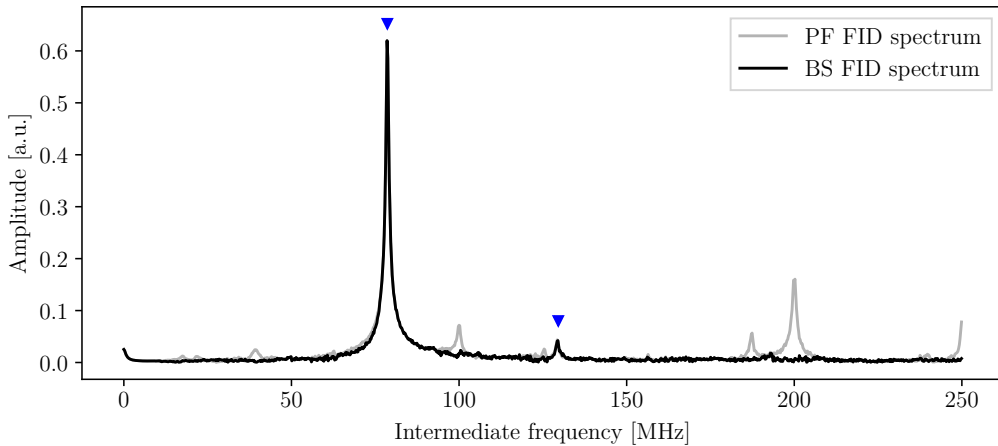


Fig. 4.15. FID spectra obtained after the pattern filter stage (gray trace) and after background subtraction (black trace). A new transition is marked at 129.4 MHz.

One must not forget however that our up-converted excitation chirp for this experiment only spans a bandwidth from 12150 to 12180 MHz, and is thus far from the frequency required to probe this new transition. A plausible cause could be the intermodulation distortion (IMD) introduced by the power amplifier.

Indeed, the power amplifier works slightly below its P3dB output power and thus generates harmonics in the output signal. If LO leakage are assumed at a frequency $f_{LO} = 12100$ [MHz] and a chirp whose instantaneous IF frequency $f_c(t)$ is ranging from 50 to 80 MHz. Then, at a given time t in the excitation sequence, the power amplifier outputs three frequencies: f_{LO} , $f_{LO} + f_c(t)$ (upper side band) and $f_{LO} - f_c(t)$ (lower side band). In the possible intermodulation products (IMPs) that cross the new transition resonant frequency $f_0 = 12229.348$ [MHz], this third-order IMP is found:

$$2(f_{LO} + f_c(t)) - f_{LO} = f_0 \quad (4.8)$$

where the solution $f_c(t) = 64.674$ [MHz] lies in the middle of the chirp IF bandwidth. Under this hypothesis, the instrument would thus be able to probe the methanol transition located at f_0 , via the third-order IMP of Eq. 4.8.

Chapter 5

Slotted waveguide in supersonic jet expansion

All the molecular experiments presented in the previous chapters have been performed in the waveguide static cell, described in Section 3.2. While this simple configuration is convenient to test and characterize the CP-FTMW spectrometer in the early stages of its development, it restricts our microwave study to molecular species that only exist at thermodynamic equilibrium and at room temperature. To extend the scientific reach of our instrument to its full potential, the CP-FTMW spectrometer is moved from the waveguide static cell to the supersonic expansion chamber of the FANTASIO experiment. [38]

In this new experimental setup, the molecular gas sample is taken from a high pressure reservoir and is introduced in the vacuum chamber, through an aperture between these two containers, referred to as the nozzle. As they enter the vacuum chamber, the molecules are cooled during the adiabatic expansion and also evolve in a collision-free molecular beam due to the sudden drop in molecular density. [39]

These characteristics of the molecular beam offer crucial features such as the simplification of the spectrum for large molecules and the possibility to form molecular clusters that play an important role in the atmospheres and interstellar media. [40, 41] Moreover, the Cavity Ringdown Spectroscopy (CRDS) experiment already implemented on the FANTASIO setup could be used along with the CP-FTMW spectrometer to perform IR-microwave double resonance experiments, [42] enlarging further the number of future potential studies.

To this date, all the CP-FTMW spectrometers in supersonic jets that have been reported in the literature employ microwave antennas to broadcast the chirped-pulse in the vacuum chamber and to collect the FID signal emitted by the molecular beam. While microwave antennas are a straightforward approach to polarize and detect molecular species in supersonic jets, the magnitude of the broadcasted electric field seen by the molecules is significantly lower than the ones that can be reached in a waveguide static cell, with the same amplifying stage.

Consequently, a power amplifier upgrade is required for antenna-based excitation if one wants to achieve the same molecular polarization that arises in waveguide cells. For cost-optimized setups such as the DDS chip-based CP-FTMW spectrometer, a

power amplifier upgrade can increase the overall cost by orders of magnitude (e.g., replacing a solid state amplifier by a traveling wave tube amplifier).

In this chapter, we present a novel approach for polarizing molecules in supersonic jets, based on a slotted waveguide directly fixed onto the nozzle and that excites the molecular beam as it passes through the waveguide, via an intake and exhaust aperture.

To this end, we first establish a theoretical reference for the performances of the horn antennas to put in perspective with the results of the slotted waveguide design. Then, the electromagnetic simulations of the slotted waveguide used to validate the optimal design are presented. Finally, the experimental setup is displayed, along with the experimental results to compare the performances of our slotted waveguides.

5.1 Theoretical considerations

The CP-FTMW spectrometers reported in the literature broadcast and detect electromagnetic radiation inside the vacuum chamber of the supersonic jet by using horn antennas. In the following, the development of the slotted waveguide is motivated by computing the on-axis mutual coupling S_{21} of the antennas shown in Fig. 5.1.

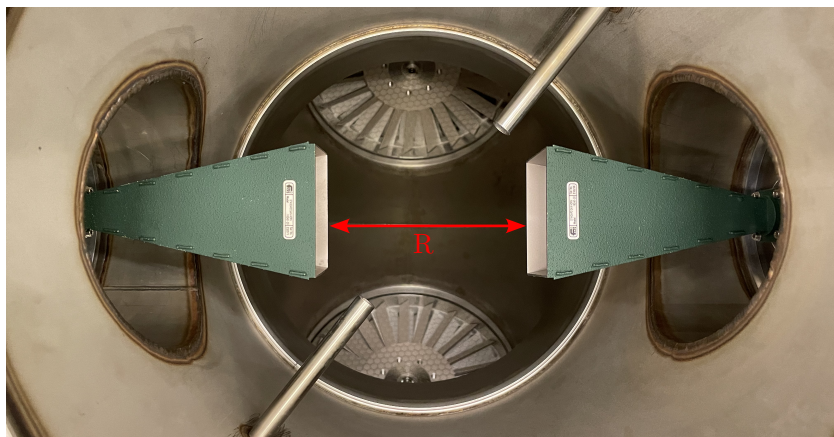


Fig. 5.1. Picture of the supersonic jet setup where the standard gain pyramidal horn antennas are mounted on lateral flanges of the vacuum chamber. The distance between the two antennas is equal to $R = 14.6$ [cm]

This configuration includes two on-axis pyramidal horn antennas with a standard gain $G = 20$ [dBi], an aperture diagonal of $D = 9.4$ [cm] and are separated by a distance $R = 14.6$ [cm]. This distance does not satisfy the far field condition for the maximum wavelength at 10 GHz, written as: [43]

$$R \gg \frac{2D^2}{\lambda} = 58 \text{ [cm]} \quad (5.1)$$

Consequently, the mutual coupling must be evaluated in the Fresnel region. A Friis formula in the Fresnel region is derived in Ref. [44]. Assuming no impedance

mismatches and no polarization mismatch, the mutual coupling is expressed as: [44]

$$S_{21} = \frac{\lambda^2}{16\pi^2 R^2} \gamma^2 G^2 = -4.6 \text{ [dB]} \quad (5.2)$$

where γ is correction term introduced to account for the Fresnel region. This mutual coupling value is used as a reference to compare with the S_{21} parameters of the slotted waveguide simulations, presented in the following section.

5.2 Electromagnetic simulations of the slotted waveguide

To outperform the horn antennas, the slotted waveguide must have a stronger polarizing electric field without compromising the gas expansion. The electromagnetic simulations presented here aim to optimize the TE_{10} electric field within the slotted waveguide. They have been conducted on the electromagnetic field simulation software **CST Studio Suite** and are based on the same WR62 rectangular waveguide which operates in the Ku-band, just as the waveguide static cell of the previous setup. This standard waveguide have fixed parameters and are shown in Table 5.1.

Table 5.1: Fixed parameters of the simulated slotted waveguide designs.

Parameter	Units	Value
length	[mm]	104.75
internal a	[mm]	15.7988
external a	[mm]	17.8308
internal b	[mm]	7.8994
external b	[mm]	9.9314
material	[-]	Copper (annealed)
electric conductivity	[S/m]	$5.8 \cdot 10^{-7}$

5.2.1 Design parameters and constraints

In the center of the structure, two slots are carved into the waveguide walls and are directly placed beneath the nozzle, as illustrated in Fig. 5.2. The slot located on the upper wall is the intake slot and has a width $w_{s,i}$. The slot placed on the lower wall is the exhaust slot and has a width $w_{s,e}$. Both slots have the same length l_s . Also, the upper wall is at a distance D from the nozzle. This distance is fixed by the mounting mechanism that fixes the waveguide to the nozzle and is assumed to be $D = 2 \text{ [mm]}$ in the remaining of this chapter. While the structure depicted in Fig. 5.2 have longitudinal slots placed on the broad walls of the waveguide, it is worth noting that other slot placements are possible, as we shall investigate later on.

In this configuration, the molecular gas is introduced into the vacuum chamber by a slit nozzle, indicated by $\mathcal{N}$ in Fig. 5.2. It then enters the waveguide through

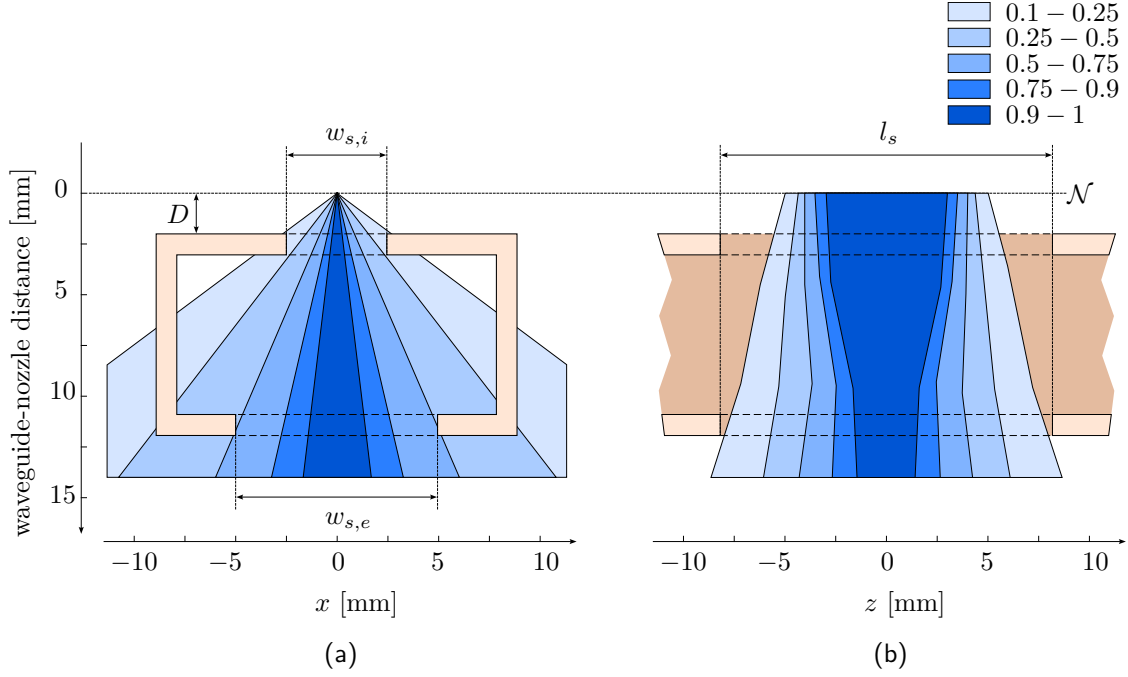


Fig. 5.2. Panel (a) shows the transverse cross section of the slotted waveguide at $z = 0$. Panel (b) shows the longitudinal cross section of the slotted waveguide at $x = 0$. The cartography of the slit nozzle expansion is reproduced from Ref. [40], where the shades of blue indicate the normalized molecular density with respect to the molecular density at $x = 0$. The slit nozzle plane is denoted by $\mathcal{N}$.

the intake slot, interacts with the EM field and finally exits through the exhaust slot. Obviously, the dimensions of the slots are constrained by the molecular beam that must cross the slotted waveguide unimpeded. We evaluate those constraints by projecting the cartography of the slit nozzle expansion established in Ref. [40] onto the slotted waveguide. We observe that the molecular beam pulsed by the slit nozzle expands mostly along the x -direction (Fig. 5.2a) and remains contained in the z -direction (Fig. 5.2b).

To preserve the free expansion along the x -axis, the width $w_{s,e}$ of the exhaust slot must be larger than the width $w_{s,i}$ of the intake slot. Along the z -axis, the length l_s of both slots can remain the same (as the expansion is restrained in the z -direction of Fig. 5.2). Unfortunately, the cartography also suggests that while the molecular beam can enter the waveguide by an appropriate choice of $w_{s,i}$, it will collide onto the inner narrow walls of the waveguide, regardless of the exhaust slot width $w_{s,e}$. Interaction between the molecular beam and the waveguide is thus unavoidable and can at least be mitigated by choosing $w_{s,e}$ as large as possible. Since the gas dynamics inside the waveguide are not simulated in this work, the expansion cartography provides a first approximation of the constraints imposed by the adiabatic expansion on the design parameters. Typical values of the design parameters displayed in Fig. 5.2 are given in Table 5.2. The length of the slot l_s is set to 35 [mm] since the current nozzle installed is longer than the one in Fig. 5.2

Table 5.2: Design parameters of the simulated slotted waveguide designs.

Parameter	value [mm]	Description
l_s	35	Length of the slots
$w_{s,i}$	5	Intake slot width
$w_{s,e}$	10	Exhaust slot width

5.2.2 Design specifications

To optimize the TE_{10} mode that propagates inside the waveguide, the slots must radiate as little microwave energy as possible. Also, the impedance mismatch at the input port of the waveguide must be low, as the reflected power diminishes the excitation electric field and could also damage the exposed power amplifier. Both of these considerations are monitored in our simulations with the S -parameters.

The most important figure of merit of the simulations is the S_{21} parameter that should be as close to 0 dB as possible. For reference, if $S_{21} < -3$ [dB] (i.e., > 3 dB insertion loss), then more than 50% of the available power delivered by the power amplifier is lost through reflection, metallic or radiation losses and therefore is not used within the waveguide to polarize the molecules. The -3 dB threshold is indicated on all the S_{21} plots presented below. Moreover, S_{11} should be as low as possible to limit the return loss but also to protect the power amplifier from the reflected power, a requirement -10 dB is thus fixed for the S_{11} .

Finally, it is desirable to preserve the Ku-band (i.e., 10-18 GHz) of the standard WR62 waveguide. To assess this criterion, the bandwidth of the simulated structures is considered as acceptable frequency range over which the S_{21} parameter is flat, within a 3 dB interval. The design specifications are gathered in Table 5.3.

Table 5.3: Design specifications of the simulated slotted waveguide designs.

Parameter	value	Description
S_{21} [dB]	$\rightarrow 0$	Power transmitted through the slotted waveguide
S_{11} [dB]	< -10	Power reflected at the waveguide input port
BW [GHz]	10-18	Covers the Ku-band, flat S_{21} within a 3 dB interval

5.2.3 Design motivations

Slotted waveguides have been extensively studied since the end of the second world war as a mean to launch microwave radiation for communication and radar applications. [45] In 1947, the theory of slots in rectangular waveguides is derived by Stevenson. [46] In his work, it is shown that radiating slots of length $\lambda_g/2$ placed in the walls of the waveguide (whose thickness is considered negligible) may be represented as series or shunt lumped elements in the equivalent transmission line circuit of the waveguide. Many configurations for the slots exist, [47] but only the ones that are compatible with the supersonic jet are reported in Fig. 5.3, namely longitudinal slots in the broad wall (case *A*) or in the narrow wall (case *B*) of the waveguide.

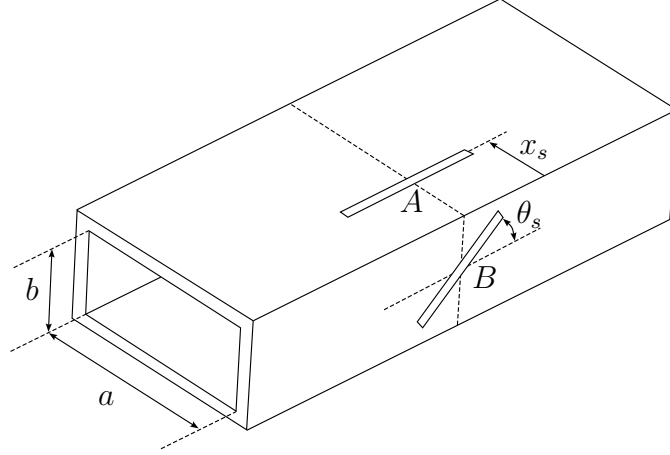


Fig. 5.3. Illustration of radiating slots, reproduced from Ref. [47].

While this formalism was primarily intended for optimizing the slotted waveguides as antennas, it is possible to exploit the same theory to achieve the exact opposite goal, that is to cancel radiation through the slots. For instance, the longitudinal slot A is modelled by a shunt element in the equivalent transmission line representation and its real part R_s follows: [46]

$$\frac{1}{R_s} \propto \cos^2 \frac{\pi x_s}{a} \quad (5.3)$$

If $x_s = a/2$ (i.e., the slot is placed at the center of the broad wall), then $1/R_s = 0$ and no power is drawn by this element, or equivalently, the slot does not radiate any power. The configuration A therefore provides a solid candidate for our simulations. On the other hand, the longitudinal slot B located on the narrow wall is also modelled as a shunt element, but its real part does not depend of the distance that separates the slot from the edge of the waveguide. Indeed, it rather depends on the angle that the slot forms with respect to the z -axis, and is given by: [46]

$$\frac{1}{R_s} \propto \cos^2 \theta_s \quad (5.4)$$

The radiation is minimized for $\theta_s = \pi/2$, which is unpractical for our application where the slots must be aligned with the waveguide, i.e., $\theta_s = 0$. For the sake of completeness, we performed the simulations of both configurations.

5.2.4 Simulation results

We present here the simulation results of the three main slotted waveguide prototypes that have been considered, from the poorest to the best performing structure. For each design, the effects of the design parameters are reviewed on the figures of merit stated earlier.

Narrow wall slots

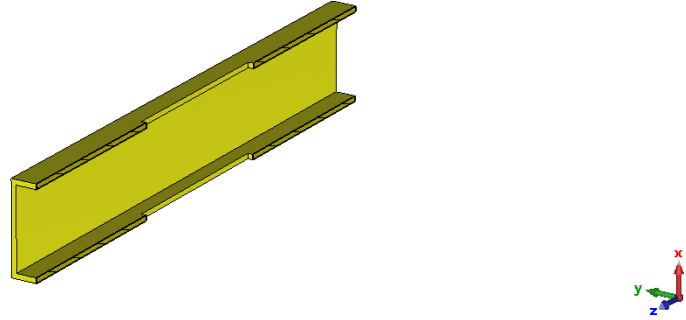


Fig. 5.4. y -plane cross section of the first version of the slotted waveguide, with the intake and exhaust slots located on the narrow wall of the waveguide.

The first simulated slotted waveguide prototype is shown in Fig. 5.4, where both slots are placed on the narrow walls of the waveguide and have a length $l_s = 35$ [mm]. The width of the exhaust slot is fixed to $w_{s,e} = 6$ [mm] while the width of the intake slot $w_{s,i}$ is swept from 2 to 6 mm. The simulated S-parameters are displayed in Fig. 5.5.

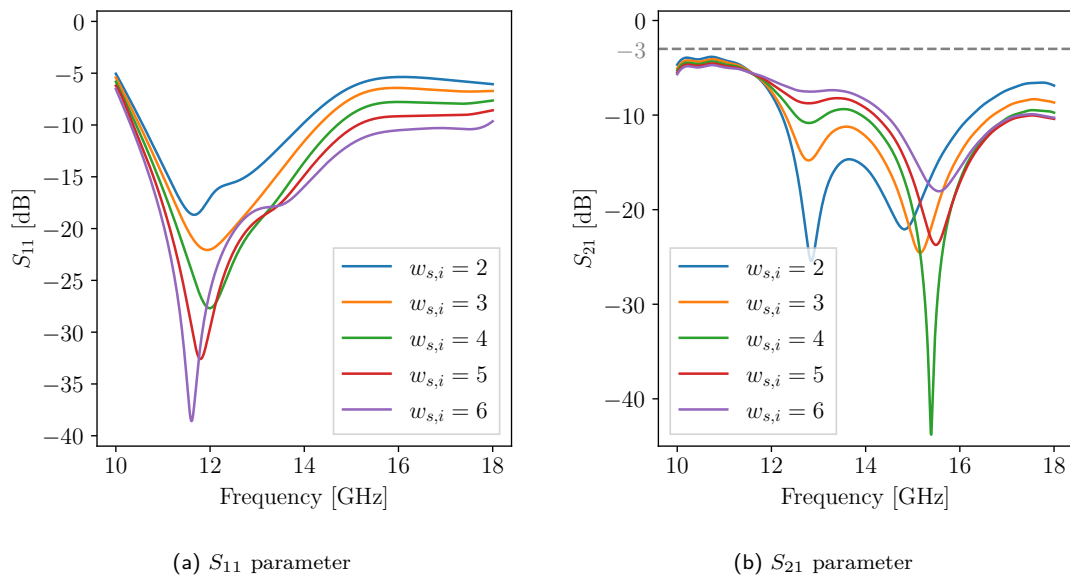


Fig. 5.5. S-parameters simulations of the narrow wall slots with $l_s = 35$ [mm], $w_{s,e} = 6$ [mm] and $w_{s,i}$ is swept from 2 to 6 mm.

Interestingly, the S_{11} parameter depicted in Fig. 5.5a improves as W_i increases which is rather counter-intuitive, as one could imagine that the S-parameters degradation increases as the size of the discontinuities become larger. On the other hand, the S_{21} parameter performs very poorly on the full TE_{10} bandwidth and for all $w_{s,i}$. At best, the S_{21} parameters reach -6 dB at 10 GHz (that is only 25% of the transmitted power kept within the waveguide) and vary downwards on the rest of the frequency range.

This result confirms that longitudinal slots on the narrow walls of the waveguide radiate the electromagnetic power contained inside the waveguide when $\theta_s = 0$. Therefore, this design will thus weakly and unevenly polarize the molecules, and cannot be considered as a viable option.

Broad wall slots

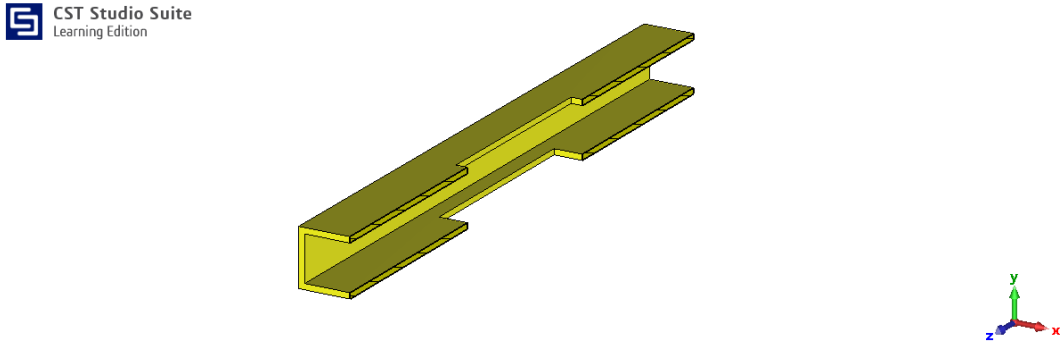


Fig. 5.6. x -plane cross section of the second version of the slotted waveguide, with the intake and exhaust slots located on the broad wall of the waveguide.

For this second prototype, both longitudinal slots are placed at the center of the broad walls of the waveguide, as shown in Fig. 5.6. The width of the exhaust slot is set to $w_{s,e} = 10$ [mm] which is the largest aperture possible to accommodate for the exiting molecular beam, without leaking too much radiation.

The S-parameter simulations are displayed in fig. 5.7, where both slots have a length of 35 [mm] and with a parametric sweep on $w_{s,i}$ that ranges from 2 to 10 mm. The S_{11} curves are acceptable for all $w_{s,i}$ where three troughs are observed and correspond to resonances occurring when the radiation happens to be maximized. Indeed, the slots can be seen as shunt elements that load the waveguide, and since a good impedance matching at the input port ensures that $Z_0 \sim Z_L^*$ (provided that the characteristic impedance Z_0 is real), the power transfer towards the load Z_L is maximized. For the S_{21} curves, a net improvement compared to results of the previous simulation are observed. The structures with $w_{s,i} = 2, 4, 6, 8$ [mm] display a 3 dB insertion loss on the 12-18 GHz frequency range. Finally, a degradation of the performances for both S-parameters are observed with the increase of $w_{s,i}$. Indeed, equation 5.3 is only valid for narrow slots and becomes irrelevant as the width of the slot approaches the width of the waveguide. [46]

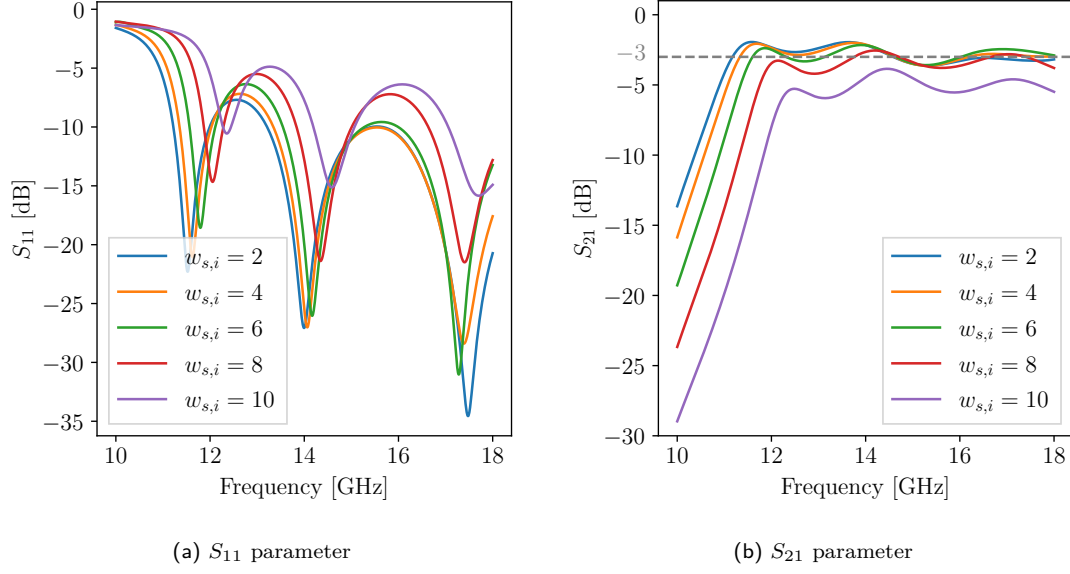


Fig. 5.7. S-parameters simulations of the broad wall slots with $l_s = 35$ [mm], $w_{s,e} = 10$ [mm] and $w_{s,i}$ is swept from 2 to 6 mm.

To determine the impact of the slot length l_s on the S-parameters, another parametric sweep is performed where l_s ranges from 30 to 50 mm, with $w_{s,i} = 6$ [mm] and $w_{s,e} = 10$ [mm].

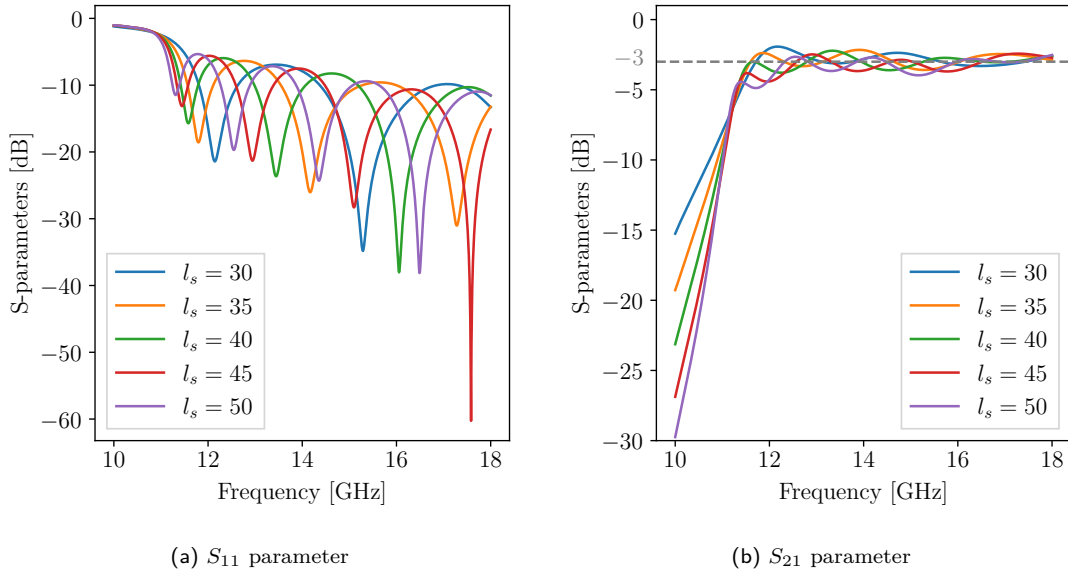


Fig. 5.8. S-parameters simulations of the broad wall slots with $w_{s,i} = 6$ [mm], $w_{s,e} = 10$ [mm] and l_s is swept from 30 to 50 mm.

As shown in Fig. 5.8, varying l_s does not change the magnitude of S_{11} or S_{12} but rather displaces the positions of the resonant frequencies, that is the positions of the troughs in S_{11} . For S_{21} , a shorter slot length seem to ease the roll-off factor below 12 GHz but the traces remain comparable in the 12-18 GHz frequency range, as they oscillate around -3 dB. Therefore, it is assumed that l_s is not a critical parameter for the EM performances of our design and should be solely chosen to accommodate for the molecular beam, as illustrated with the expansion cartography

of Fig. 5.2b. In the remaining of the simulations, we keep $l_s = 35$ [mm] to tolerate larger slit expansion along the z -direction.

Broad wall slots with tapers

CST Studio Suite
Learning Edition

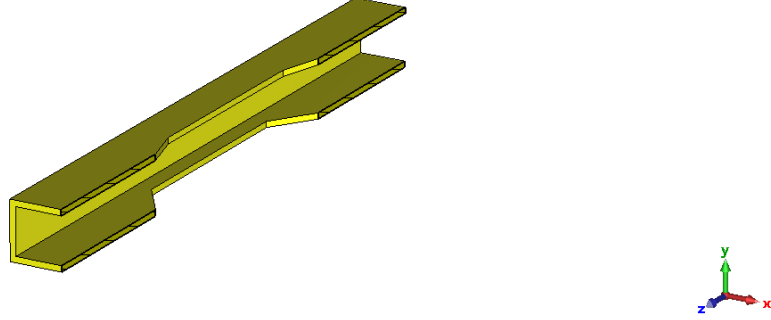


Fig. 5.9. x -plane cross section of the third version of the slotted waveguide. The intake and exhaust slots are located on the a -wall of the waveguide, with tapers.

The last prototype displayed in Fig. 5.9 aims to enhance the previous design by adding $\lambda_g/4$ tapers on both ends of each slot. We choose the central frequency of the target bandwidth at 14 GHz to fix the length $l_{s,t}$ of the tapers with $l_{s,t} = \lambda_g/4 = 7.29$ [mm]. Both intake and exhaust slots have now a total length of $l_s + 2l_{s,t} = 49.58$ [mm]. Once again, $w_{s,e} = 10$ is kept constant and a parametric sweep is conducted on $w_{s,i}$ that ranges from 2 to 10 mm, as displayed in Fig. 5.10.

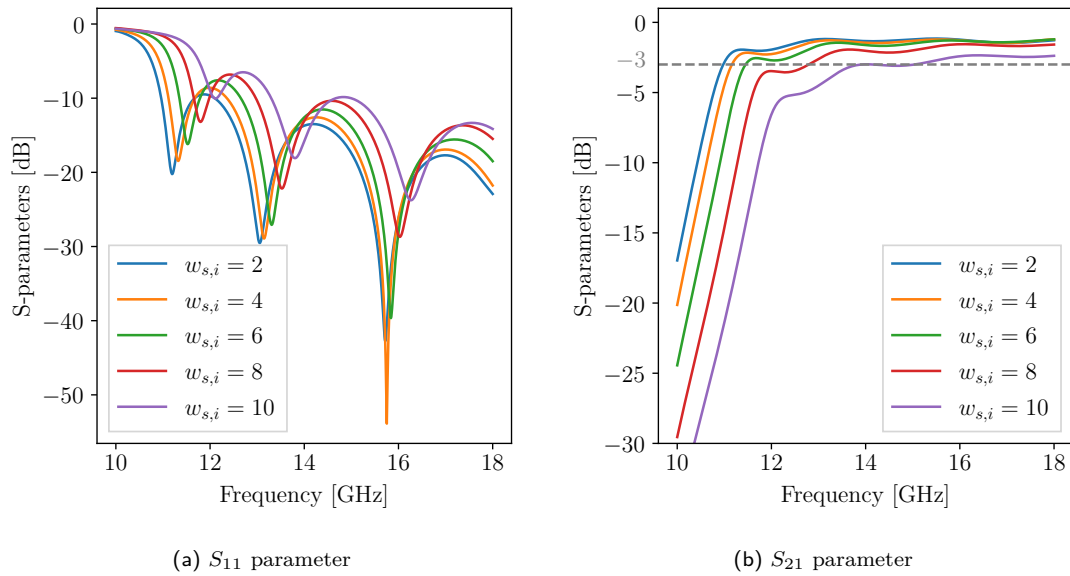


Fig. 5.10. S-parameters simulations of the broad wall slots with $l_s = 35$ [mm], $w_{s,e} = 10$ [mm] and $w_{s,i}$ is swept from 2 to 10 mm. The tapers have a length $\lambda_g/4 = 7.29$ [mm]

The tapers seem to have a significant effect on the S-parameters where the S_{11} curves are shifted downwards compared to the previous structure. For the S_{21}

traces, the figures are greatly improved where the structures with $w_{s,i} = 2, 4, 6$ [mm] are located around -1.5 dB on the 12-18 GHz bandwidth, that is 70% of microwave power kept within the waveguide. Furthermore, flat S_{21} curves are observed which is ideal to polarize evenly the molecules and thus to provide accurate relative intensities. Finally, The larger intake widths display above -3 dB performances above 13 GHz for $w_{s,i} = 8$ [mm] and above 14 GHz for $w_{s,i} = 10$ [mm].

This last slotted waveguide is chosen as the optimal design and its parameters are displayed in Table. 5.4.

Table 5.4: Selected design parameters for the slotted waveguide structure.

Parameter	value [mm]	Description
$w_{s,i}$	2(10)	Intake slot width
$w_{s,e}$	10	Exhaust slot width
l_s	35	Length of the slots
$l_{s,t}$	7.29	Length the tapers

This design is expected to have an insertion loss below 3 dB over the 12-18 GHz frequency range and a return loss above 10 dB (i.e, less than 10% of reflected power towards the power amplifier). It is worth noting that the fabricated slotted waveguide has been modified during this master thesis, where the intake slot has been widen to $w_{s,i} = 10$ [mm] for reasons which are stated at the end of this chapter. The width of the intake slot waveguide is thus explicitly given in each result below to discern the two variations.

5.3 Results

The results are divided in two parts with first the S-parameters measurements required to validate the simulations and the spectra obtained in the supersonic jet for both the horn-antenna and the slotted waveguide configurations.

5.3.1 S-parameters measurements

To validate the simulation results of the selected design of table. 5.4, with $w_{s,i} = 10$ [mm], we measured the S-parameters of this slotted waveguide prototype with a Vector Network Analyzer (VNA) at the Wallonia Electronics & Communications Measurements (WELCOME) facilities. The VNA measurements are compared with the simulation results in Fig. 5.11.

Overall, a good fit between the experimental VNA measurements and the results of the CST simulations are observed. In Fig. 5.11a, the same three troughs are recognized in both the simulation and in the experimental measurement. In Fig. 5.11b, the measured S_{21} parameter is slightly lower than the simulated S_{21} . This slight decrease can be attributed to the additional insertion losses caused by the two SMA/WG adaptor flanges that were used during the VNA measurements but not taken into account in the simulations. Those flanges are also used in the

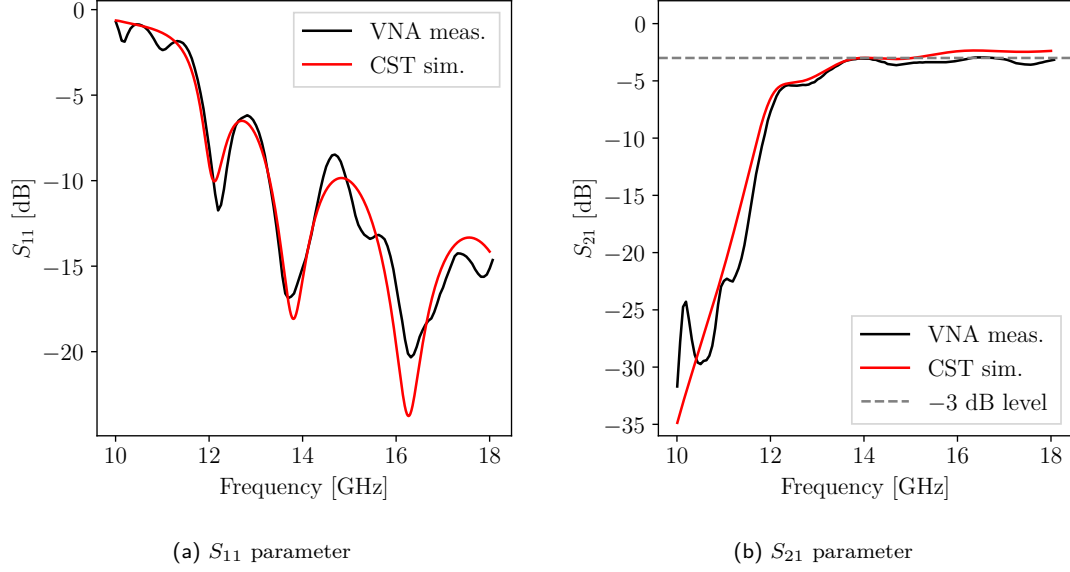


Fig. 5.11. S-parameters comparison between the VNA measurements (black traces) and the CST simulations (red traces) with the S_{11} comparison on panel (a) and the S_{21} comparison on panel (b). The -3 dB level is indicated on the latter panel for reference.

supersonic jet experiment and seem to have negligible insertion losses. Based on those results, it is concluded that the CST simulations are a reliable technique to evaluate the RF performance of our slotted waveguide designs. However, beyond the quality of the fit, the experimental results also confirm the very poor performances of the slotted waveguide in the 10-14 GHz frequency range and the nearly -3 dB plateau on the second half of TE_{10} mode bandwidth, as shown in Fig. 5.11. At best, we can claim for 50% of the available power delivered by the power amplifier in the 14-18 GHz frequency range.

Finally, the S_{21} parameter obtained with this prototype is higher by 1.6 [dB] than the mutual coupling computed for the horn antennas. While it thus at least shows the superiority of the waveguide in terms of transmitted power, it is by no means a sufficient condition to claim a sensitivity gain for the molecular spectra.

In an attempt to replicate the presence of the metallic body of the nozzle which is normally in close contact with the waveguide during operation in the supersonic expansion chamber, the intake slot of the waveguide has been covered with a metallic plate. In Fig. 5.12, the S-parameters measurements are compared between the unimpeded slotted waveguide (2 slots) and the case where the upper slot is covered (1 slot).

The presence of the metallic plate significantly improves both the S_{11} and the S_{21} parameters. For the latter parameter, the 3 dB cutoff frequency is lowered to 12 GHz and a plateau of -2 dB is reached in the 13-18 GHz frequency range, where 68 % of the power delivered by the power amplifier is transmitted through the slotted waveguide. This result suggests that the metallic body of the nozzle could reduce the insertion loss of the slotted waveguide. For a future work, one could also imagine to integrate the metallic body of the nozzle into the slotted waveguide to minimize the radiation emitted by the upper slot, and thus the insertion loss.

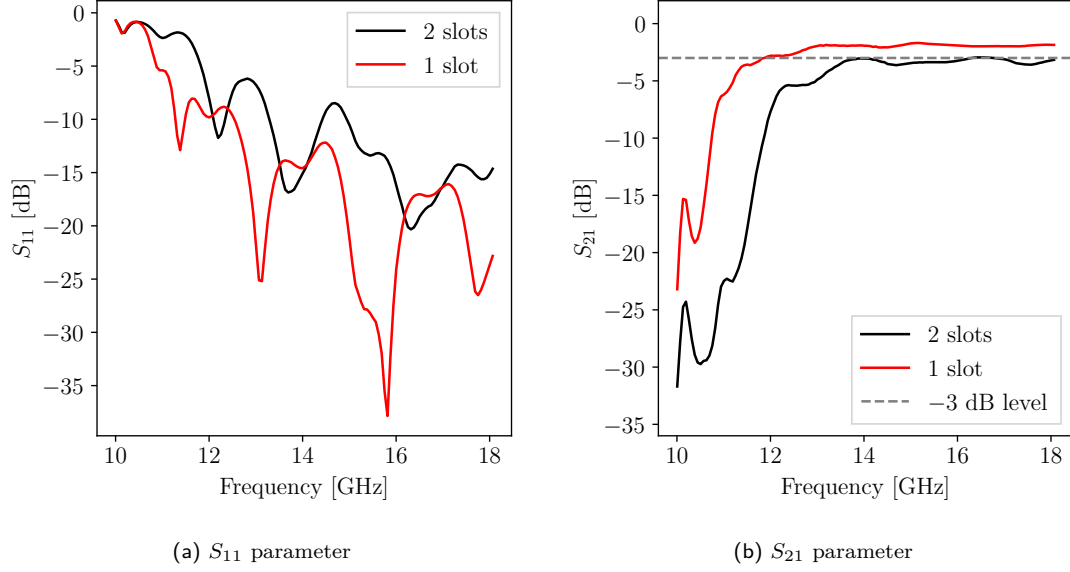


Fig. 5.12. S-parameters comparison of the unimpeded slotted waveguide (black trace) and the slotted waveguide where the upper slot is covered (red trace), with the S_{11} parameter in panel (a) and the S_{21} parameter in panel (b). The -3 dB level is indicated on the latter panel for reference.

5.3.2 Spectra

The newly fabricated slotted waveguide prototype (with $w_{s,i} = 2$ [mm]) is now fully characterized and can be installed in the supersonic jet setup. The prototype is fixed onto the nozzle using the mounting mechanism designed and fabricated at the mechanical workshop of the NAPS department, as illustrated in Fig.5.13.

To finalize the experimental setup of our CP-FTMW spectrometer in a supersonic jet, the nozzle apparatus displayed on the picture above is sealed into the vacuum chamber of the FANTASIO experiment. The semi-rigid SMA cables dangling from the SMA/WG adaptors are connected to the excitation and the detection modules of the spectrometer via vacuum-tight SMA feedthroughs placed in two flanges of the vacuum chamber.

During the design stage of the slotted waveguide, one of our main concern was the perturbation of the expansion due to collisions of the molecular beam with the waveguide. Indeed, according to the cartography of the slit expansion, [40] the molecular beam is expected to collide with the inner walls and could result as a dramatic reduction in rotational cooling.

To confirm or infirm this hypothesis, one should probe a molecular transition that is only detectable at high temperature, such a transition is therefore called a hot transition. Consequently, if this hot transition appears on our spectrum, we would know for certain that the expansion has been corrupted to an extent where the cooling property of the expansion is severely mitigated. Conversely, a molecular transition that is enhanced at low temperature is referred to as a cold transition. If this cold transition displays a weak SNR in the spectrum, then it would also suggest that a perturbation of the adiabatic expansion occurred.

It happens that the two methanol transitions that were identified at 12178.584

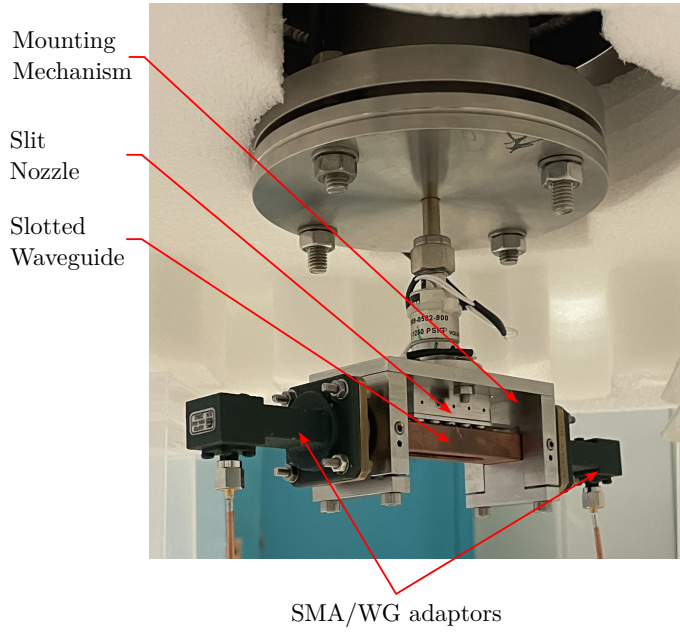


Fig. 5.13. Picture of the supersonic jet setup while the nozzle system is outside of the vacuum chamber. The slotted waveguide is directly fixed onto the nozzle using a mounting mechanism.

MHz and 12229.348 MHz in Fig. 4.15 are a cold and a hot transition, respectively. Those transitions can therefore be used to perform the experiment announced in the previous paragraph. To probe those two transitions, the methanol sample and an argon carrier gas are mixed together and then introduced continuously (i.e., in a CW regime) by the slit nozzle through the waveguide. Two experiments are conducted to probe the cold and the hot transition and one other is performed without any molecular gas to collect the background spectrum. The corresponding spectrometer settings are given in table. 5.5.

Table 5.5: Spectrometer settings for the three CW methanol expansion experiments.

transition	f_0 [MHz]	f_{LO} [MHz]	f_{chirp} [MHz]	N_{av}
cold transition	12178.584	12300	113 $\rightarrow$ 123	10^6
hot transition	12229.348	12300	62 $\rightarrow$ 72	10^6
background	-	12300	62 $\rightarrow$ 72	10^6

It is worth noting that in those experiments, the transitions are probed with the LSB of the up-converted chirp. For instance, the cold transition is polarized when $f_{LO} - f_{chirp} = f_0$ and gives the resonant intermediate frequency $f_{chirp} = f_{LO} - f_0 = 121.416$ [MHz] (for the hot transition, the resonant intermediate frequency is $f_{chirp} = 70.652$ [MHz]).

In Fig. 5.14, the resulting spectra of the three experiments of table. 5.5 are displayed. All spectra contain 10^6 averages and have been processed with the pattern filter. In the red trace, which is associated to the hot transition experiment, a spectral line is marked by the red triangle at the exact hot transition resonant intermediate frequency of 70.652 MHz. Since it does not appear in the two other spectra, this

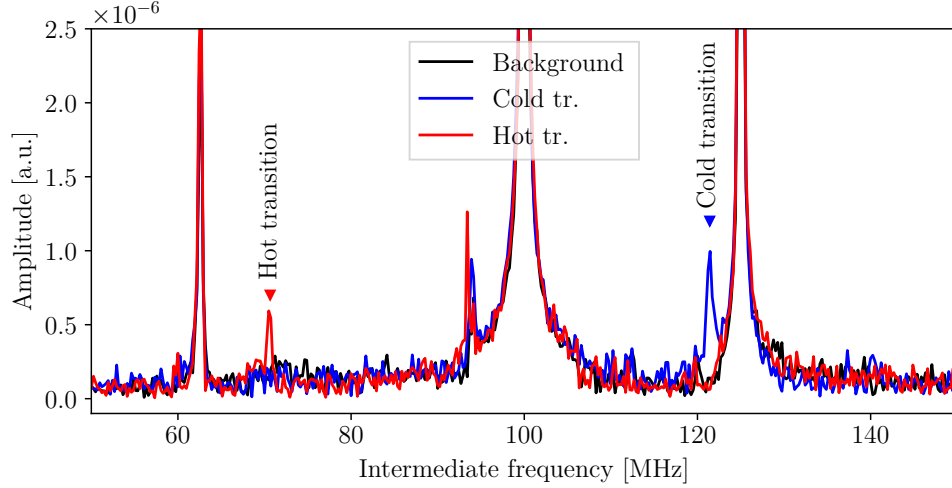


Fig. 5.14. Spectra resulting from the three CW methanol expansion experiments detailed in table. 5.5

line is assigned to the hot transition and therefore confirms that the rotational cooling resulting from the adiabatic expansion did not occur. Similarly, the cold transition assigned in the blue trace displays a signal strength comparable to the hot transition which does match the expected results.

5.3.3 Discussion

The results presented in Fig. 5.14 suggest that the expansion is perturbed by the slotted waveguide, where the prototype used for this experiment has an intake slot of width $w_{s,i} = 2$ [mm]. Consequently, it has been decided to modify the slotted waveguide by increasing the width of the intake slot to 10 mm, and to perform the same experiment in order to evaluate a potential improvement. Unfortunately, this experiment has not been reproduced due to technical difficulties and time constraints.

However, the cartography of the supersonic jet displayed in Fig. 5.2 suggests that the molecular beam may collide with the interior walls of the waveguide while the molecular beam should have sufficient clearance to enter the intake slot unperturbed. Based on those observations, it is concluded that better gas dynamics may occur if a skimmer is placed on the nozzle of the supersonic jet to select the innermost region of the molecular beam. Furthermore, it is possible that the S_{21} parameter of the slotted waveguide improves if the metallic skimmer is placed in close contact with the intake slot of the waveguide, as suggested by the VNA measurements performed with metallic plate covering the intake slot, shown in Fig. 5.12.

Chapter 6

Conclusion and perspectives

The focus of this master thesis was the design, characterization and the validation of the first chirped-pulse Fourier transform spectrometer of the UCLouvain.

To begin with, the non-working CP-FTMW spectrometer which was previously built based on the design of Finneran *et al.* [3] has been troubleshooted. To this end, all the elements of the spectrometer have been characterized and the timing of the instrument was carefully reviewed. To obtain the first molecular signal, the instrument was installed on a waveguide static cell, inside which a methanol sample gas was introduced. The first molecular spectrum produced with the instrument has been obtained with the strongest methanol rotational transition present in the 10-18 GHz frequency range.

Then, major improvements have been obtained in terms of sensitivity, evaluated with the benchmark methanol transition. A reduction of the noise emitted during the detection sequence was achieved thanks to the presence of the blanking switch. It allowed to observe the FID in the time domain, after $32 \cdot 10^3$ averages and with an acquisition rate of ~ 50 Hz. To further increase the sensitivity of the instrument, the DAQ rate has been increased by leveraging the large memory of the HS5 USB digitizer with a fast averaging scheme program, developed during this work. It is now possible to acquire 10^6 FIDs in less than 9 minutes, which would have taken more than 5 hours with the previous oscilloscope.

This increase in sensitivity also revealed a large spurious content which has been addressed with a custom post-processing pipeline. Periodic features introduced by the various clocks of the instrument have been removed with the iterative pattern filter (PF) while the remaining high frequency transients have been treated with an in-phase local background subtraction (BS). Most of the spurs have been successfully removed which allows for an accurate assignment of the rotational transitions present in the spectrum.

Finally, a new slotted waveguide design has been proposed to polarize the molecular beam and detect the transient emission in supersonic jet conditions. The slotted waveguide has been developed with the aim of maximizing the electric field contained inside the structure while ensuring that the expansion of the molecular beam is not perturbed by the presence of the waveguide. The selected optimum design was fabricated and tested with a VNA to confirm the quality of the simulations. Both

the simulations and the VNA measurements display a 3 dB insertion loss over the 14-18 GHz frequency range. Despite its good electromagnetic performances, poor sensitivity have been reported in the resulting spectra. Based on the cartography of the supersonic jet, it has been shown that the molecular beam may collide with the inside walls and induce a significant collision frequency.

Perspectives for experimental improvements: For the CP-FTMW instrument to reach its full potential, many directions may be considered to improve the current design:

- In this work, the bandwidth of the current digitizer is limited to 250 MHz and the LO frequency has to be adjusted manually to reach a specific segment of the Ku-band. To scan the full 10-18 GHz frequency in a continuous fashion, a segmented CP-FTMW must be implemented. During this thesis, a rudimentary version of a segmented CP-FTMW LabView controller has been developed. The completion of this software would allow to perform broadband spectra acquisitions.
- The current limitation to the fast averaging scheme developed for the USB oscilloscope is the slow transfer time due to the USB2.0 protocol. However, the fast averaging software developed for the USB oscilloscope can be used with any digitizer which provides a large acquisition memory. Therefore, this limitation may be mitigated by replacing the USB oscilloscope with an ADC card which is directly coupled to a Field Programmable Gate Array (FPGA), onto which the data acquisitions are directly collected in an accumulator buffer [28].
- While the DDS of the spectrometer have been thoroughly investigated, some small discrepancies occur between the chirp parameters and the actual duration of the chirp observed on the oscilloscope. Currently, the DDS is operated with the evaluation software provided by Analog Devices which obscures the low-level functioning of the DDS. A low-level control of the DDS with an Arduino or any integrated RTOS (real time operating system) would help to investigate the exact behavior of the chirp generation. Moreover, the better control of the DDS would also allow to create more complex pulse sequences (e.g. nutation experiments [35]). Finally, the control of the DDS with an integrated computer would constitute a step further towards the integration of the instrument.
- The sensitivity of the instrument may also be enhanced with RF components upgrades. The first one is the replacement of the current power amplifier for at least a 40 dBm amplifier. The other RF upgrade would be to consider the removal of the PIN diode limiter at the input of the detection module. Indeed, the consecutive insertion losses of the PIN diode limiter and the detection switch contribute largely to the noise figure of detection chain.
- While no positive spectra have been obtained with the slotted waveguide in the supersonic jet so far, there is still a lot of room for improvement to better accommodate the molecular beam inside the waveguide. A promising strategy

would be to better integrate the slit nozzle into the waveguide and to control the expansion of the beam with a skimmer. Such a solution would allow to improve both the electromagnetic performance of the slotted waveguide and the gas dynamics inside the structure.

It is one hope that in the near future, this CP-FTMW spectrometer will be involved in other experiments in UCLouvain as:

- The FANTASIO experiment, to perform the structure determination of large molecules or weakly bound clusters formed in the supersonic jet, e.g., water complexes. [48, 49]
- The buffer gas cooling, where chemical and mechanistic studies could take place. [50, 51]

Another perspective is to decrease further the footprint and power consumption of the spectrometer to study *in situ* the atmosphere.

Bibliography

- [1] Gordon G. Brown, Brian C. Dian, Kevin O. Douglass, Scott M. Geyer, and Brooks H. Pate. The rotational spectrum of epifluorohydrin measured by chirped-pulse fourier transform microwave spectroscopy. *Journal of Molecular Spectroscopy*, 238(2):200–212, 2006.
- [2] Gordon G. Brown, Brian C. Dian, Kevin O. Douglass, Scott M. Geyer, Steven T. Shipman, and Brooks H. Pate. A broadband fourier transform microwave spectrometer based on chirped pulse excitation. *Review of Scientific Instruments*, 79(5):053103, 2008.
- [3] Ian A. Finneran, Daniel B. Holland, P. Brandon Carroll, and Geoffrey A. Blake. A direct digital synthesis chirped pulse fourier transform microwave spectrometer. *Review of Scientific Instruments*, 84(8):083104, 2013.
- [4] Amanda Steber. Millimeter wave and microwave instrumental development for analytical and astrochemical applications, 11 2014.
- [5] Luyao Zou, Roman A. Motiyenko, Laurent Margulès, and Eugen A. Alekseev. Millimeter-wave emission spectrometer based on direct digital synthesis. *Review of Scientific Instruments*, 91(6):063104, 2020.
- [6] Dassault Systèmes. Cst studio suite, <https://www.3ds.com/fileadmin/products-services/simulia/products/cst/simulia-cst-studio-suite-brochure.pdf>.
- [7] Jens-Uwe Grabow. *Fourier Transform Microwave Spectroscopy Measurement and Instrumentation*. John Wiley & Sons, Ltd, 2011.
- [8] P.F. Bernath. *Spectra of Atoms and Molecules*. Oxford University Press, 2005.
- [9] C.J. Foot and D.P.C.J. Foot. *Atomic Physics*. Oxford Master Series in Physics. OUP Oxford, 2005.
- [10] P.T. Ho and J. Weiner. *Light-Matter Interaction: Fundamentals and Applications*. Number vol. 1. Wiley, 2008.
- [11] C. Cohen-Tannoudji, B. Diu, and F. Laloe. *Mécanique Quantique - Tome 2: Nouvelle édition*. EDP sciences, 2018.
- [12] H. Dreizler. Experiences with microwave fourier transform spectroscopy of molecular gases. *Molecular Physics*, 59(1):1–28, 1986.
- [13] P.A. Rinck. *Magnetic Resonance in Medicine: A Critical Introduction*. Books on Demand, 2019.

- [14] Rao Sathyanarayan. Numerical solution to optical bloch equation for a two level atom using runge kutta method, 2015.
- [15] E. L. Hahn. Spin echoes. *Phys. Rev.*, 80:580–594, Nov 1950.
- [16] Richard P. Feynman, Frank L. Vernon, and Robert W. Hellwarth. Geometrical representation of the schrödinger equation for solving maser problems. *Journal of Applied Physics*, 28(1):49–52, 1957.
- [17] G. Barratt Park and Robert W. Field. Perspective: The first ten years of broadband chirped pulse fourier transform microwave spectroscopy. *The Journal of Chemical Physics*, 144(20):200901, 2016.
- [18] J. C. McGurk, T. G. Schmalz, and W. H. Flygare. Fast passage in rotational spectroscopy: Theory and experiment. *The Journal of Chemical Physics*, 60(11):4181–4188, 1974.
- [19] R. H. Romer and R. H. Dicke. New technique for high-resolution microwave spectroscopy. *Phys. Rev.*, 99:532–536, Jul 1955.
- [20] T. J. Balle and W. H. Flygare. Fabry–perot cavity pulsed fourier transform microwave spectrometer with a pulsed nozzle particle source. *Review of Scientific Instruments*, 52(1):33–45, 1981.
- [21] T. J. Balle, E. J. Campbell, M. R. Keenan, and W. H. Flygare. A new method for observing the rotational spectra of weak molecular complexes: Krhcl. *The Journal of Chemical Physics*, 71(6):2723–2724, 1979.
- [22] Jens-Uwe Grabow, Wolfgang Stahl, and Helmut Dreizler. A multioctave coaxially oriented beam-resonator arrangement fourier-transform microwave spectrometer. *Review of Scientific Instruments*, 67(12):4072–4084, 1996.
- [23] Steven T. Shipman and Brooks H. Pate. *New Techniques in Microwave Spectroscopy*. John Wiley & Sons, Ltd, 2011.
- [24] John J. Spokas and Charles P. Slichter. Nuclear relaxation in aluminum. *Phys. Rev.*, 113:1462–1472, Mar 1959.
- [25] David Schmitz, V. Alvin Shubert, Thomas Betz, and Melanie Schnell. Multi-resonance effects within a single chirp in broadband rotational spectroscopy: The rapid adiabatic passage regime for benzonitrile. *Journal of Molecular Spectroscopy*, 280:77–84, 2012. Broadband Rotational Spectroscopy.
- [26] Ken B. Cooper, Robert J. Dengler, Nuria Llombart, Bertrand Thomas, Goutam Chattopadhyay, and Peter H. Siegel. Thz imaging radar for standoff personnel screening. *IEEE Transactions on Terahertz Science and Technology*, 1(1):169–182, 2011.
- [27] Mariyam Fatima, Cristóbal Pérez, Benjamin E. Arenas, Melanie Schnell, and Amanda L. Steber. Benchmarking a new segmented k-band chirped-pulse microwave spectrometer and its application to the conformationally rich amino alcohol isoleucinol. *Phys. Chem. Chem. Phys.*, 22:17042–17051, 2020.

- [28] Justin L. Neill, Brent J. Harris, Amanda L. Steber, Kevin O. Douglass, David F. Plusquellic, and Brooks H. Pate. Segmented chirped-pulse fourier transform submillimeter spectroscopy for broadband gas analysis. *Opt. Express*, 21(17):19743–19749, Aug 2013.
- [29] Analog Device Inc. *2.5 GSPS Direct Digital Synthesizer with 12-Bit DAC*, 9 2022. Rev. G.
- [30] Ian A. Finneran, Daniel B. Holland, P. Brandon Carroll, and Geoffrey A. Blake. Supplementary material of a direct digital synthesis chirped pulse fourier transform microwave spectrometer. *Review of Scientific Instruments*, 84(8):083104, 2013.
- [31] D.M. Pozar. *Microwave Engineering, 4th Edition*. Wiley, 2011.
- [32] Ferenc Marki, Christopher Marki, and Ph. D. microwave mixer basics primer a tutorial for rf & microwave mixers.
- [33] The Cologne Database for Molecular Spectroscopy. Methanol line list: <https://cdms.astro.uni-koeln.de/cgi-bin/cdmssearch?file=c032504.cat>.
- [34] The Cologne Database for Molecular Spectroscopy. derivation of the quantum numbers for methanol: <https://cdms.astro.uni-koeln.de/cgi-bin/cdmsinfo?file=e032504.cat>.
- [35] G. Barratt Park, Adam H. Steeves, Kirill Kuyanov-Prozument, Justin L. Neill, and Robert W. Field. Design and evaluation of a pulsed-jet chirped-pulse millimeter-wave spectrometer for the 70–102 ghz region. *The Journal of Chemical Physics*, 135(2):024202, 2011.
- [36] Steven W. Smith. *The Scientist and Engineer’s Guide to Digital Signal Processing*. California Technical Publishing, USA, 1997.
- [37] Brian M. Hays, Théo Guillaume, Thomas S. Hearne, Ilsa R. Cooke, Divita Gupta, Omar Abdelkader Khedaoui, Sébastien D. Le Picard, and Ian R. Sims. Design and performance of an e-band chirped pulse spectrometer for kinetics applications: Ocs – he pressure broadening. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 250:107001, 2020.
- [38] M. Herman, K. Didriche†, D. Hurtmans, B. Kizil, P. Macko, A. Rizopoulos, and P. Van Poucke. Fantasio: a versatile experimental set-up to investigate jet-cooled molecules. *Molecular Physics*, 105(5-7):815–823, 2007.
- [39] Richard E. Smalley, Lennard Wharton, and Donald H. Levy. Molecular optical spectroscopy with supersonic beams and jets. *Accounts of Chemical Research*, 10(4):139–145, 1977.
- [40] K Didriche. *High resolution infrared spectroscopy: setting up an experiment to investigate small clusters (Unpublished doctoral dissertation)*. Bruxelles, 2008.

- [41] Daniel P. Zaleski, Justin L. Neill, Matt T. Muckle, Nathan A. Seifert, P. Brandon Carroll, Susanna L. Widicus Weaver, and Brooks H. Pate. A ka-band chirped-pulse fourier transform microwave spectrometer. *Journal of Molecular Spectroscopy*, 280:68–76, 2012. Broadband Rotational Spectroscopy.
- [42] Brian C. Dian, Gordon G. Brown, Kevin O. Douglass, and Brooks H. Pate. Measuring picosecond isomerization kinetics via broadband microwave spectroscopy. *Science*, 320(5878):924–928, 2008.
- [43] S. J. Orfanidis. *Electromagnetic Waves and Antennas*. 2016.
- [44] Ilkyu Kim. Electromagnetic computation of the short-range wireless linkbudget for biomedical communication. In Kok Yeow You, editor, *Emerging Microwave Technologies in Industrial, Agricultural, Medical and Food Processing*, chapter 4. IntechOpen, Rijeka, 2018.
- [45] Jiro Hirokawa and Miao Zhang. *Waveguide Slot Array Antennas*, pages 1389–1413. Springer Singapore, Singapore, 2016.
- [46] A. F. Stevenson. Theory of slots in rectangular wave-guides. *Journal of Applied Physics*, 19(1):24–38, 1948.
- [47] Phillip N. Richardson and Hung Yuet Yee. Design and analysis of slotted waveguide antenna arrays. *Microwave Journal*, 31:109, June 1988.
- [48] Richard J. Saykally and David J. Wales. Pinning down the water hexamer. *Science*, 336(6083):814–815, 2012.
- [49] Cristóbal Pérez, Daniel P. Zaleski, Nathan A. Seifert, Berhane Temelso, George C. Shields, Zbigniew Kisiel, and Brooks H. Pate. Hydrogen bond cooperativity and the three-dimensional structures of water nonamers and decamers. *Angewandte Chemie International Edition*, 53(52):14368–14372, 2014.
- [50] Sandra Eibenberger, John M. Doyle, and David Patterson. Enantiomer-specific state transfer of chiral molecules. *Physical review letters*, 118 12:123002, 2017.
- [51] Jessica P. Porterfield, Sandra Eibenberger, David Patterson, and Michael C. McCarthy. The ozonolysis of isoprene in a cryogenic buffer gas cell by high resolution microwave spectroscopy. *Phys. Chem. Chem. Phys.*, 20:16828–16834, 2018.

UNIVERSITÉ CATHOLIQUE DE LOUVAIN
École polytechnique de Louvain

Rue Archimède, 1 bte L6.11.01, 1348 Louvain-la-Neuve, Belgique | www.uclouvain.be/epl