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Modelisation of a gas phase polarization induced by a 200 GHz chirped pulse

R. Bocquet[1], D. Fontanari[1], C. Bray[1], G. Mouret[1], A. Cuisset[1], G. Dhont[1], K. Hickson[2] and F. Hindle[1]

[1]LPCA, Université du Littoral Côte d'Opale, 59140 Dunkerque, France, robin.bocquet@univ-littoral.fr

[2]Institut des Sciences Moléculaires, Université de Bordeaux, Talence, F-33400, France

Introduction

A millimeter wave chirped pulse spectrometer (mmWCP) has been developed to study chemical reactivity at low temperature using the CRESU technique **[1]**. The project goal is to detect and quantify gas species created during reactivity at thermodynamic conditions close to interstellar media, requiring the combination of the 2 techniques cited above. The first part of the project, undertaken at the LPCA, is the realization and the development of the mmWCP operating between 190 - 210 GHz **[2]**. One of the interests of this instrument is its capability to simultaneously and rapidly measure numerous molecular transitions of different species in gas phase by probing individual rotational transitions. However, during the trials of the experiment, we were confronted with the difficulty of determining the rotational line intensities according to their position within the chirped pulse. For this reason, we have undertaken a theoretical study to get obtain an analytical expression for the detected signal as a function of the line position in the pulse.

Experimental set up

A mmWCP instrument operates in 2 phases. The first is the polarization of the gas under study by the CP source. The second phase is the recording the Free Induction Decay (FID) signal after extinction of the CP source.

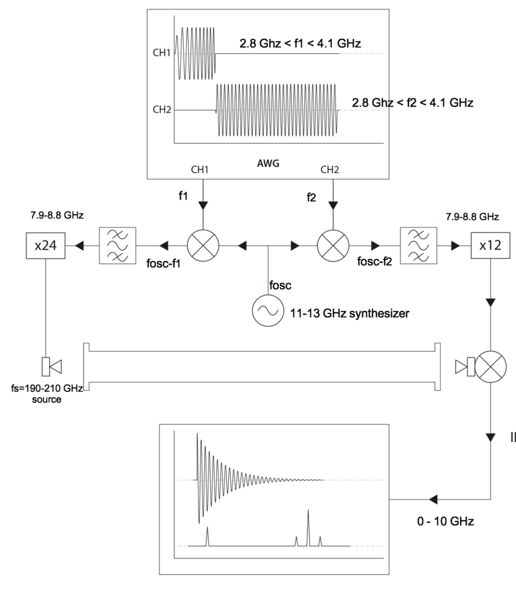


Fig. 1. mmWCP experiment

The mmWCP is generated by mixing the AWG CH1 with a fixed oscillator before being frequency-multiplied to the 190 to 210 GHz range. It is launched into free space using a diagonal horn antenna and propagated through the sample chamber. A second diagonal horn antenna is used to couple the molecular FID signal to the sub-harmonic mixer. The other ports of the mixer are used to provide the local oscillator (LO) signal and extract the intermediate frequency (IF). The IF signal is recorded using a fast oscilloscope while being triggered by a timing signal generated by the AWG. A large number of measurement cycles are averaged before applying a FFT to obtain the spectrum. The experiment can detect line intensities of the order of 10^{-26} cm^{-1}/molec.cm^{-2} in few seconds and has the possibility to scan over 10 GHz in one shot **[2]**.

Theory

Polarization phase - The measured molecular signal is proportional to the gas polarization at the end of the chirped pulse T_c. At this stage we used the optical Bloch equations **[3, 4]** to describe the evolution of an isolated molecular system for which 2 energy levels |a> and |b> are probed. We will suppose that the system is submitted to an electric field **E** with a linear time dependent pulsation:

The optical Bloch equations are then given by :

$$\begin{aligned} \mathring{z}(t) &= -(\tau_2 + i\omega_0) z(t) - i\varepsilon(t) W(t) \\ \mathring{W}(t) &= -\tau_1 (W(t) - W_{eq}) + \frac{1}{2i} (\varepsilon^*(t) z(t) - \varepsilon(t) z^*(t)) \end{aligned} \quad (1)$$

$$\varepsilon(t) = \Omega_0 \mathrm{e}^{-i[(\omega_0 - c\Delta\omega)t + \frac{\Delta\omega}{2T_c} t^2]} \quad (2)$$

$$\Omega_0 = \frac{\mu_{ab} . E_0}{\hbar} \quad \text{and} \quad \omega(t) = \omega_0 - c\Delta\omega + \frac{\Delta\omega}{T_c} t \quad (3)$$

where z(t) is the polarization, W(t) the difference population of the 2 levels, W_{eq} the difference at the thermodynamic equilibrium, τ_1 and τ_2 are the inverse of relaxation times of levels and dipoles respectively, Ω_0 is the Rabi frequency, T_c is the duration of the chirp, c is a unitless parameter describing the molecular resonance position in the chirped pulse (0<c<1 and $\omega(cT_c) = \omega_0$) and $\Delta\omega$ is the pulsation extension of the chirp.

In order to find a solution, at least in a first approximation, we solve in the equations (1) the one containing $\mathring{z}(t)$ while considering W(t) given, and the other one while considering z(t) given. Two uncoupled first-order differential equations are therefore obtained providing a general formulation of the solution. Then, considering the initial conditions (z(0)=0 and W(0)=W_{eq}), we have

$$\begin{aligned} z(t) &= -i \int_0^t e^{-(i\omega_0 + \tau_2)(t-x)} \varepsilon(x) W(x) dx \\ W(t) &= W_{eq} + \frac{1}{2i} \int_0^t e^{-\tau_1 (t-x)} (\varepsilon^*(x) z(x) - \varepsilon(x) z^*(x)) dx \end{aligned} \quad (4)$$

We can write the 2 functions as series:

$$z(t) = z^{(0)}(t) + z^{(1)}(t) + z^{(2)}(t) + \ldots$$
$$W(t) = W^{(0)}(t) + W^{(1)}(t) + W^{(2)}(t) + \ldots$$

and find the solutions by successive approximations:

$$\begin{aligned} z^{(n+1)}(t) &= -i\int_0^t e^{-(i\omega_0+\tau_2)(t-x)}\varepsilon(x)W^{(n)}(x)\,dx \\ W^{(n+1)}(t) &= \frac{1}{2i}\int_0^t e^{-\tau_1(t-x)}(\varepsilon^*(x)z^{(n)}(x)-\varepsilon(x)z^{(n)*}(x))\,dx \end{aligned} \quad (5)$$

Taking the initial conditions (z(0)=0 and W(0)=W_{eq}), only the odd terms of the z-series and the even terms of the W-series remain. We will work with $z^{(1)}(t)$ and $W^{(0)}(t)=W_{eq}$ and do a changing variable to simplify the equations (rotating frame):

$$\xi^{(1)}(t)=z^{(1)}(t)e^{i[(\omega_0-c\Delta\omega)t+\frac{\Delta\omega}{2T_c}t^2]} \quad (6)$$

Then we can show that for t=T_c :

$$\xi^{(1)}(T_c)\approx\rho_{app}e^{i\theta_{app}}+\tilde{\xi} \quad (7)$$

with

$$\begin{aligned} \rho_{app} &= \frac{\sqrt{2\pi}\,\Omega_0 W_{eq}}{\sqrt{\Delta\omega}}\sqrt{T_c}\exp[\frac{-T_c}{T_2}(1-c)] \\ \theta_{app} &= (1-c)^2\frac{\Delta\omega}{2}T_c-\frac{3}{4}\pi \\ \tilde{\xi} &= \frac{W_{eq}\Omega_0}{\Delta\omega}(\frac{1}{1-c}+\frac{1}{c}\exp[i\frac{\Delta\omega}{2}T_c(1-2c)])\exp[\frac{-T_c}{T_2}(1-c)] \end{aligned} \quad (8)$$

ρ_{app} (which is positive) represents the amplitude of $\zeta^{(1)}(T_c)$, θ_{app} its phase and $\tilde{\xi}$ induces a small oscillation. In particular ρ_{app}, tends to 0 when T_c tends to 0, increases until it reaches a maximum when $T_c=\frac{T_2}{2(1-c)}$ with value $\frac{\sqrt{2\pi}}{e}\frac{\sqrt{T_c}}{\Delta\omega}W_{eq}\Omega_0$ and then it decreases toward 0 as $T_c\rightarrow+\infty$. The approximation which retains ρ_{app} is already very good to describe the system behavior.

Free Induction Decay (FID) – In this phase, the Rabi frequency vanishes and the optical Bloch equations simplify **[3]**. Using an heterodyne detection scheme, we can demonstrate that the output signal is :

$$S(t')=B\sqrt{\frac{T_c}{\Delta\omega}}e^{\frac{-T_c}{T_2}(1-c)}[e^{\frac{-t'}{T_2}-\frac{t'^2\Delta\omega_D^2}{4}}\cos(\omega_{IF}t'+\Phi)] \quad (9)$$

where $t'=t-T_c$ and B is a constant depending of the experiment (amplifiers, mixers …). Applying a FFT, we can access the signal amplitude at the intermediate frequency:

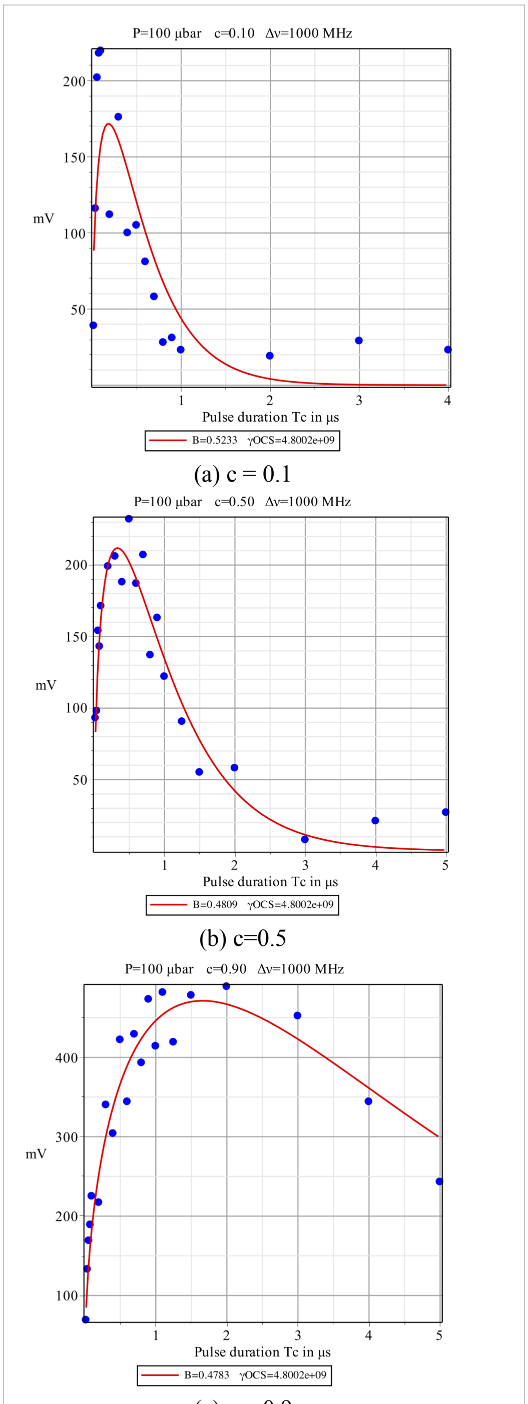
$$A_{TF}(\nu_{IF})=\frac{B}{\sqrt{\Delta\omega}}\sqrt{T_c}\exp[\frac{-T_c}{T_2}(1-c)] \quad (10)$$

Experimental results

We compared the theoretical model we obtained with experimental data recorded with carbonyl sulfide gas (OCS). We chose the 17->16 rotational line centered at 206.745 GHz. The output signal amplitude at the IF have been measured for different gas pressure and different positions of the molecular resonance in the CP described by the c parameter. The figure 2 compares experimental measurements and analytical modelisations for 3 different c values. A very good agreement is obtained between experimental data (blue points) and model (red curve) for a 1 GHz extension chirp and for a 100 µbar gas pressure (collisional width larger than Doppler width).

Conclusion

We used a mathematical method by successive approximations to solve the optical Bloch equations and to get an analytical formula giving the output signal of a chirped pulse experiment. This will be useful for absolute intensity lines measurements and to optimize the pulse duration to obtain the best signal to noise ratio.



(a) c = 0.1

(b) c=0.5

(c) c = 0.9

Fig. 2. Output signal amplitude $A_{TF}(\nu_{IF})$, function of pulse duration T_c, recorded for OCS at 206.745 GHz with line resonance position c as parameter. Comparison of experimental data (blue points) and model (red curve) from equation (10)

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