

Molecules probed with a slow chirped-pulse excitation: Analytical model of the free-induction-decay signal

D. Fontanari, C. Bray, G. Dhont, G. Mouret, A. Cuisset, F. Hindle, and R. Bocquet^{*}
LPCA, Université du Littoral Côte d'Opale, 189A Avenue Maurice Schumann, 59140 Dunkerque, France

K. M. Hickson
ISM, Université de Bordeaux, 351 Cours de la Libération, 33405 Talence Cedex, France



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Most chirped-pulse experiments refer to a theoretical study from McGurk, Schmalz, and Flygare [*J. Chem. Phys.* **60**, 4181 (1974)] which is well tailored to interpret the signals obtained with very fast chirped pulses, but is not sufficient to account for the signals in the case of slower chirped pulses used in spectroscopy to increase the signal-to-noise ratio. A theoretical study of the polarization of molecules subjected to a chirped pulse in a cell, uniform supersonic flow, or molecular beam is presented. Three degrees of approximation for the polarization are introduced and are compared with the numerical solution of the optical Bloch equations. These expressions enter the analytic expression of the free-induction-decay signal which is validated against experimental data on the rotational emission spectra of OCS molecules. A relation among the pulse duration, the line position in the chirped pulse, and the signal amplitude is proposed in the thermalized case. It assists in the optimization of the chirped-pulse parameters and in the estimation of the error associated with the line intensity.

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I. INTRODUCTION

Chirped-pulse (CP) spectrometers are now widely employed at microwave and millimeter frequencies to perform high-resolution spectroscopic studies [1–5]. A small number of instruments have also been set up in the submillimeter band [6]. Such systems employ a two-step measurement cycle. First, the gas being studied is polarized by a CP emitted from a powerful source. Second, after the source extinction, the emission of the molecules corresponding to the free induction decay (FID) is recorded. The signal level is proportional to the polarization reached at the end of the CP. The spectrum of the molecular emission is then recovered by the use of a Fourier transform. The broadband nature of CP spectroscopy has the advantage that many rotational transitions may be probed simultaneously and can be used as a new means to produce input data for quantitative spectroscopy or chemical kinetics experiments [7] if the relative intensities of the transitions are reliable.

While this technique is very well suited to the frequency measurement of rotational transitions, measurements of line strengths require more care. It has already been shown that the position of the rotational transition frequency in the pulse can affect the measured intensity, especially in cases where pulse durations are increased to obtain sufficient signal-to-noise ratios [5,8]. However, most groups use a model originally developed by McGurk *et al.* [9] to model FID signals. It neglects re-emission effects during the pulse, together with population and coherence relaxation times, due to a very fast passage on the transition. In the model, the polarization at

the end of the pulse is proportional to $\sqrt{T_c/\Delta\omega}$, where T_c is the pulse duration and $\Delta\omega$ is the spectral extension of the CP. This behavior is in contradiction with the experimental measurements for which we observe a maximum FID signal for a particular pulse duration [5].

This work proposes analytical expressions for the polarization which will be helpful to analyze the experiments with slower CP. Section II deals with the polarizing step where the molecules evolve under the influence of the CP. We propose three approximations and compare them with the numerical integration of the optical Bloch equations. Both thermalized cases (cell and high-density uniform supersonic flow achieved with Laval nozzles) and nonthermalized cases (molecular beam) are discussed. Section III presents the second step of a CP experiment, i.e., the free induction decay. The results of Sec. II are leveraged to propose an analytical expression of the FID recorded signal. This formula is validated through comparison with experimental data in the thermalized case using an experimental setup described in Ref. [5], similar to experimental setups of Refs. [2,4,6,10]. We show how to use this expression to optimize the amplitude of the signal and to take into account the dependence of the intensity on the line position.

II. ANALYTICAL EXPRESSION OF THE POLARIZATION IN A CP EXPERIMENT

A. Optical Bloch equations

The molecular interaction with an electromagnetic wave has been extensively described in the literature [9,11–14]. We discuss for simplicity a two-level isolated molecular system, given by its energy levels E_a and E_b with $E_a - E_b = \hbar\omega_0$. We

^{*}robin.bocquet@univ-littoral.fr

consider the interaction between this two-level system and an electromagnetic field with the angular frequency $\omega(t)$. The system of N molecules with a transition dipole moment, μ_{ab} , is described by the evolution of its density matrix. Introducing the relaxation mechanisms by $\gamma_1 = 1/T_1$ and $\gamma_2 = 1/T_2$ (respectively, the inverse of the decay time of the population difference and the inverse of the dipole dephasing time) and W_{eq} , the population difference at thermodynamic equilibrium, we get the following generic forms of the optical Bloch equations:

$$\begin{aligned} \frac{dz}{dt}(t) &= -(\gamma_2 + i\omega_0)z(t) - i\mathcal{E}(t)W(t), \\ \frac{dW}{dt}(t) &= -\gamma_1[W(t) - W_{\text{eq}}] + \frac{1}{2i}[\mathcal{E}^*(t)z(t) - \mathcal{E}(t)z^*(t)], \end{aligned} \quad (1)$$

where $W(t)$ and $z(t) = \mathcal{P}(t)/(N\mu_{ab})$ correspond to the difference of population and the pseudopolarization, respectively, with $\mathcal{P}(t)$ being the polarization. The function $\mathcal{E}(t) = e^{-i\alpha(t)}\Omega_0$ represents the perturbation of the system with $\Omega_0 = \frac{\mu_{ab}E_0}{\hbar}$ being the Rabi frequency and $\alpha(t)$ being a generic function of time. Equations (1) and (2) are solved for the given functions $W(t)$ and $z(t)$, respectively. Using the general solution of a first-order differential equation, we have

$$\begin{aligned} z(t) &= z(0)e^{-(i\omega_0+\gamma_2)t} - i \int_0^t e^{-(i\omega_0+\gamma_2)(t-x)} \mathcal{E}(x)W(x)dx, \\ W(t) &= W_{\text{eq}} + [W(0) - W_{\text{eq}}]e^{-\gamma_1 t} \\ &\quad + \frac{1}{2i} \int_0^t e^{-\gamma_1(t-x)} [\mathcal{E}^*(x)z(x) - \mathcal{E}(x)z^*(x)]dx. \end{aligned} \quad (2)$$

We suppose that $z(t)$ and $W(t)$ may be written as series:

$$\begin{aligned} z(t) &= z^{(0)}(t) + z^{(1)}(t) + z^{(2)}(t) + \dots, \\ W(t) &= W^{(0)}(t) + W^{(1)}(t) + W^{(2)}(t) + \dots \end{aligned} \quad (3)$$

Replacing these series in Eqs. (3) and (4) and identifying term by term, we find the series recurrences:

$$\begin{aligned} z^{(n+1)}(t) &= -i \int_0^t e^{-(i\omega_0+\gamma_2)(t-x)} \mathcal{E}(x)W^{(n)}(x)dx, \\ W^{(n+1)}(t) &= \frac{1}{2i} \int_0^t e^{-\gamma_1(t-x)} [\mathcal{E}^*(x)z^{(n)}(x) - \mathcal{E}(x)z^{(n)*}(x)]dx. \end{aligned} \quad (4)$$

B. Mathematical formulation

We consider a linear CP with the duration T_c and the spectral extension $\Delta\omega$. The CP frequency equals the molecular resonance at time r_0T_c with $r_0 \in [0; 1]$, the relative line position in the CP (for $r_0 = \frac{1}{2}$ the chirp is centered on the resonance ω_0). The angular frequency is given by

$$\omega(t) = \frac{d\alpha}{dt}(t) = \omega_0 - r_0\Delta\omega + \frac{\Delta\omega}{T_c}t. \quad (5)$$

Except for free-induction-decay or double-resonance experiments, we are dealing with $z(0) = 0$. Only the odd terms of the z series and the even terms of the W series are nonzero. In

particular, the first nonzero terms of the series are

$$\begin{aligned} z^{(1)}(t) &= -i \int_0^t e^{-(i\omega_0+\gamma_2)(t-x)} \mathcal{E}(x)W^{(0)}(x)dx, \\ W^{(0)}(t) &= W_{\text{eq}} + [W(0) - W_{\text{eq}}]e^{-\gamma_1 t}. \end{aligned} \quad (6)$$

A rotating-wave approximation is performed by introducing $\xi^{(n)}(t) = e^{i\alpha(t)}z^{(n)}(t)$. If we define $\beta^2 = \frac{\Delta\omega}{T_c}$, the sweep speed of the pulse, the pseudopolarization is then given by

$$\xi^{(1)}(t) = W_{\text{eq}}g(t, \gamma_2) + [W(0) - W_{\text{eq}}]e^{-\gamma_1 t}g(t, \gamma_2 - \gamma_1), \quad (7)$$

where

$$g(t, \gamma) = -i\Omega_0 \int_0^t e^{-\gamma(t-x)-ic\beta^2(t-x)T_c+i\frac{\beta^2}{2}(t^2-x^2)}dx, \quad (8)$$

which can be integrated using the error function

$$g(t, \gamma) = \rho(t, \gamma)e^{i\theta(t, \gamma)}\sigma(t, \gamma), \quad (9)$$

where

$$\begin{aligned} \rho(t, \gamma) &= \frac{\sqrt{\pi}\Omega_0}{\sqrt{2}\beta} \exp[-\gamma(t - r_0T_c)], \\ \theta(t, \gamma) &= (t - r_0T_c)^2 \frac{\beta^2}{2} - \frac{3}{4}\pi - \frac{\gamma^2}{2\beta^2}, \\ \sigma(t, \gamma) &= \text{erf}\left[\frac{e^{i\frac{\pi}{4}}}{\sqrt{2}}\left(r_0T_c\beta - i\frac{\gamma}{\beta}\right)\right] \\ &\quad + \text{erf}\left[\frac{e^{i\frac{\pi}{4}}}{\sqrt{2}}\left((t - r_0T_c)\beta + i\frac{\gamma}{\beta}\right)\right]. \end{aligned} \quad (10)$$

At time $t = T_c$ (polarization at the end of the pulse), we can simplify the expressions by ignoring small terms ($\frac{\gamma}{\beta} \ll 1$) and taking a first-order asymptotic expansion of the error function [15] in order to obtain

$$g_{\text{asy}}(T_c, \gamma) = \rho_{\text{asy}}(T_c, \gamma)e^{i\theta_{\text{asy}}(T_c)} + g_{\text{osc}}(T_c, \gamma), \quad (11)$$

where

$$\begin{aligned} \rho_{\text{asy}}(T_c, \gamma) &= \frac{\sqrt{2\pi}\Omega_0}{\sqrt{\Delta\omega}}\sqrt{T_c} \exp[-T_c(1 - r_0)\gamma], \\ \theta_{\text{asy}}(T_c) &= (1 - r_0)^2 \frac{\Delta\omega}{2}T_c - \frac{3}{4}\pi, \\ g_{\text{osc}}(T_c, \gamma) &= \frac{\Omega_0}{\Delta\omega} \left[\frac{1}{1 - r_0} + \frac{1}{r_0} \exp\left(i\frac{\Delta\omega}{2}T_c(1 - 2r_0)\right) \right] \\ &\quad \times \exp[-T_c(1 - r_0)\gamma]. \end{aligned} \quad (12)$$

If we use Eq. (9), $\xi^{(1)}(T_c)$ is then approximated by

$$\begin{aligned} \xi_{\text{asy}}^{(1)}(T_c) &= W_{\text{eq}}g_{\text{asy}}(T_c, \gamma_2) \\ &\quad + [W(0) - W_{\text{eq}}]e^{-\gamma_1 T_c}g_{\text{asy}}(T_c, \gamma_2 - \gamma_1). \end{aligned} \quad (13)$$

The term $g_{\text{osc}}(T_c, \gamma)$ induces an oscillation whose amplitude decreases as T_c and/or $\Delta\omega$ increases. We neglect it to get an approximation of the pseudopolarization:

$$\begin{aligned} \xi_{\text{app}}^{(1)}(T_c) &= e^{i\theta_{\text{asy}}(T_c)} \{W_{\text{eq}}\rho_{\text{asy}}(T_c, \gamma_2) \\ &\quad + [W(0) - W_{\text{eq}}]e^{-\gamma_1 T_c}\rho_{\text{asy}}(T_c, \gamma_2 - \gamma_1)\}. \end{aligned} \quad (14)$$

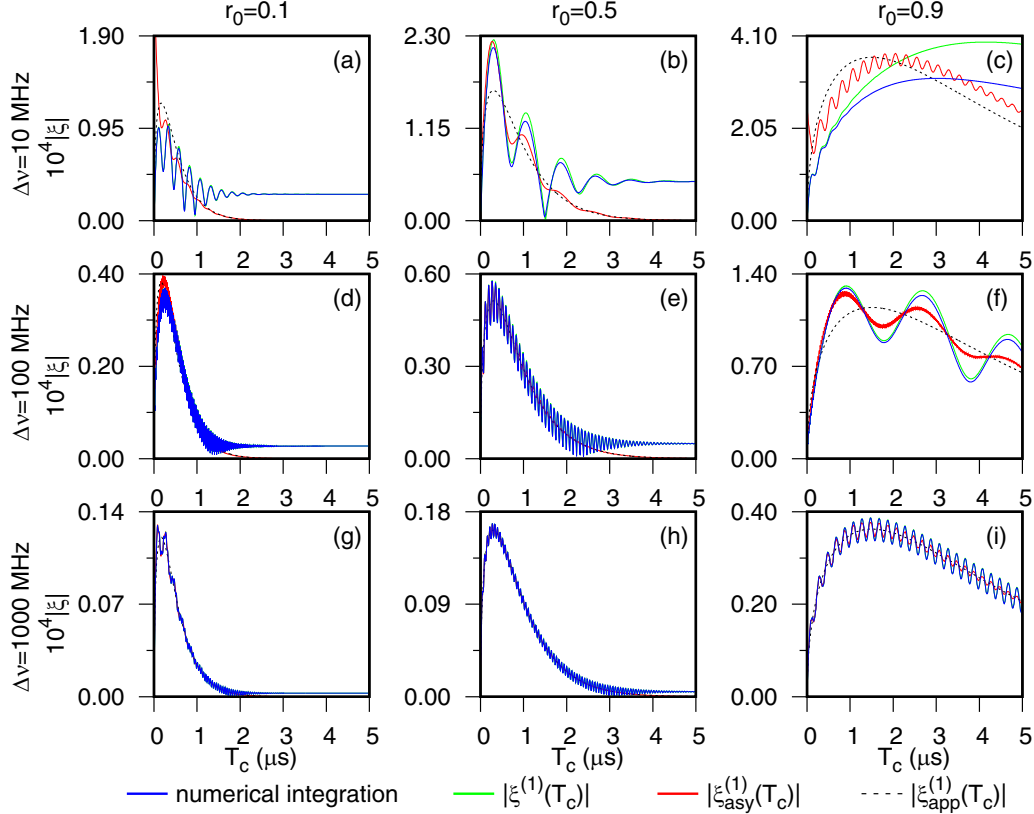


FIG. 1. Polarization modulus at the end of the CP against the chirp duration T_c for the $J = 17 \rightarrow 16$ rotational transition of OCS at 206.745 GHz. $|\xi^{(1)}(T_c)|$ is the first nonzero term of the series, $|\xi_{\text{asy}}^{(1)}(T_c)|$ is the asymptotic expansion and $|\xi_{\text{app}}^{(1)}(T_c)|$ is the last approximation of the polarization. The parameters are $\Omega_0 = 2.4$ rd/ μs , $W(0) = W_{\text{eq}} = 6 \times 10^{-4}$, and $T_2 = T_1 = 0.3$ μs . The first, second, and third columns correspond to $r_0 = 0.1, 0.5$, and 0.9 . The first, second, and third rows correspond to $\Delta\nu = 10, 100$, and 1000 MHz.

Finally, the modulus of the pseudopolarization is approximated by $|\xi(T_c)| \approx |\xi^{(1)}(T_c)| \approx |\xi_{\text{asy}}^{(1)}(T_c)| \approx |\xi_{\text{app}}^{(1)}(T_c)|$, with

$$|\xi_{\text{app}}^{(1)}(T_c)| = \sqrt{2\pi}\Omega_0 \sqrt{\frac{T_c}{\Delta\omega}} e^{-\frac{T_c}{T_2}(1-r_0)} \times |W_{\text{eq}} + [W(0) - W_{\text{eq}}]e^{-\frac{T_c}{T_1}r_0}|, \quad (17)$$

which is the product of three terms. The first one corresponds to the polarization in the McGurk *et al.* approximation [9]. The second one describes an exponential decay with relaxation time T_2 , for a duration of $T_c(1 - r_0)$ (the duration between the line position and the end of the pulse). The third term represents the relaxation of the difference population towards the equilibrium with the relaxation time T_1 , for the duration $r_0 T_c$ (the duration between the beginning of the pulse and the line position).

C. Numerical validation of the approximations

Figure 1 compares the three approximations ($|\xi^{(1)}(T_c)|$, $|\xi_{\text{asy}}^{(1)}(T_c)|$, $|\xi_{\text{app}}^{(1)}(T_c)|$) of the modulus of the polarization with the numerical integration of the optical Bloch equations using a Rosenbrock method [16] for three different spectral extensions and three different line positions r_0 . We consider a two-level system consisting of the $J = 16$ and $J = 17$ rotational levels of the OCS molecule with $W(0) = W_{\text{eq}}$ and $T_2 = T_1 = 0.3$ μs . We notice that except for the case $\Delta\nu = 10$ MHz

and $r_0 = 0.9$ of Fig. 1(c), the first approximation $|\xi^{(1)}(T_c)|$ given by Eq. (9) reproduces the numerical integration. As soon as $\Delta\nu \geq 100$ MHz, the curves corresponding to the second approximation $|\xi_{\text{asy}}^{(1)}(T_c)|$ [Eq. (15)] are acceptable. The curves corresponding to the third approximation $|\xi_{\text{app}}^{(1)}(T_c)|$ [Eq. (16)] have no oscillations and reproduce the global behavior of the numerical results, in particular the optimal pulse duration and the corresponding value of the polarization. Figure 1 suggests however two remarks. First, the asymptote of the modulus of the polarization for high T_c value is not zero. This effect is seen for $r_0 \leq 0.5$ and would be visible at $T_c > 10$ μs for $r_0 = 0.9$. This asymptote decreases when $\Delta\nu$ increases and/or r_0 decreases. Second, for $\Delta\nu = 1000$ MHz, the amplitude of the oscillations decreases from $r_0 = 0.1$ to $r_0 = 0.5$ but increases from $r_0 = 0.5$ to $r_0 = 0.9$.

D. Discussion

The molecules interacting with a chirped pulse can be probed under different experimental conditions: in an ordinary cell [5,17,18], in a uniform supersonic flow [8], or in a molecular beam [2,3,19]. We can take advantage of the typical characteristics of each experimental setup summed up in Table I to adapt the analytic approximation (17) of the modulus of the polarization obtained in Sec. II B.

In an ordinary cell or in a uniform supersonic flow, the molecules are thermalized. The rotational temperature may

TABLE I. Characteristic parameters for three experimental setups. The simplified modulus of polarization (see text) and the optimal duration $T_{c,\max}$ for the maximum signal are reported. T_{rot} is the molecular rotational temperature.

Thermodynamic cond.	Thermalized case		Nonthermalized case
Experiment	Ordinary cell	Uniform supersonic flow	Molecular beam
T_{rot}	300 K	10–150 K	5–10 K
T_2		$\approx T_1$	$< T_1$
$W(0)$		$W_{\text{eq}}(T_{\text{rot}})$	$\gg W_{\text{eq}}(300 \text{ K})$
$ \xi_{\text{app}}^{(1)}(T_c) $		$\sqrt{2\pi}\Omega_0\sqrt{\frac{T_c}{\Delta\omega}} W_{\text{eq}}(T_{\text{rot}}) e^{-\frac{T_c}{T_2}(1-r_0)}$	$\sqrt{2\pi}\Omega_0\sqrt{\frac{T_c}{\Delta\omega}} W(0) $
$T_{c,\max}$		$\frac{T_2}{2(1-r_0)}$	—

be the ambient temperature in the former situation while it is lowered to a few dozens of kelvin in the latter one. In both cases, the relaxation time T_2 is of the same order of magnitude as T_1 and the initial population difference $W(0)$ corresponds to its equilibrium value $W_{\text{eq}}(T_{\text{rot}})$. Under these conditions, the analytic approximation of Eq. (17) is proportional to $|W_{\text{eq}}(T_{\text{rot}})|$, which can be significantly increased in a uniform supersonic flow with respect to an ordinary cell at 300 K by decreasing the temperature. The pulse duration giving the maximal polarization is found to be $T_{c,\max} = T_2/[2(1-r_0)]$, which depends on T_2 but not on T_1 .

The behavior of experiments in the nonthermalized case is different. In a molecular beam experiment, the rotational temperature is lowered to a few kelvin and the collisional linewidth is strongly reduced, implying generally $T_2, T_1 \gg T_c$ [14,20]. Under these conditions, the analytic approximation of Eq. (17) simplifies to $\sqrt{2\pi}\Omega_0\sqrt{\frac{T_c}{\Delta\omega}}|W(0)|$ (see Table I) and thus reduces to the McGurk *et al.* model [9], which is a monotonously increasing function of the pulse duration. The molecular beam chirped-pulse setup is very advantageous in terms of the signal-to-noise ratio. First, the signal is enhanced by the initial difference populations $W(0)$ which can be increased by 1 or 2 orders of magnitude compared to the difference population in an ordinary cell at 300 K. Second, the duration of the FID signal increases due to the relaxation time T_2 (see III) to such an extent that the decay of the FID signal is often driven by the Doppler inhomogeneous broadening (see Appendix A). The Doppler width is indeed proportional to ω_0 [see Eq. (A5)] and more pronounced in the millimeter or submillimeter ranges than in the microwave range. Unfortunately, the drawback of a molecular beam experiment is a limited operating frequency range due to the peaked shape of the population of energy levels towards the low J values [21].

III. FREE-INDUCTION-DECAY SIGNAL

A. Mathematical formulation

The source extinction occurs at $t = T_c$. The emission of the polarized molecules which evolve freely is observed with time $t' = t - T_c$. The polarization in the rotating-wave approximation $\tilde{\mathcal{P}}(t')$ is given by (see Appendix A)

$$\tilde{\mathcal{P}}(t') = N\mu_{ab}\xi(T_c)\exp\left[-\frac{t'}{T_2} - \frac{t'^2\Delta\omega_D^2}{4\ln 2}\right], \quad (18)$$

where $\Delta\omega_D$ is the Doppler width. The electric field is emitted at the angular frequency ω_0 , the molecular resonance, with an

amplitude proportional to the polarization module [2]:

$$E(t') \propto |\tilde{\mathcal{P}}(t')|e^{-i(\omega_0 t' + \phi)} + \text{c.c.} \quad (19)$$

Chirped-pulse experiments use a heterodyne detection scheme [5] where a local oscillator of angular frequency ω_{LO} is used to shift the spectrum from ω_0 to the intermediate angular frequency $\omega_{\text{IF}} = \omega_0 - \omega_{\text{LO}}$. If ϕ is a phase term at the time origin, the output signal is (see Appendix B)

$$S(t') \propto N\mu_{ab}|\xi_{\text{app}}^{(1)}(T_c)|e^{-\frac{t'}{T_2}}e^{-\frac{t'^2\Delta\omega_D^2}{4\ln 2}}\cos(\omega_{\text{IF}}t' + \phi). \quad (20)$$

The exponential terms describe dampings respectively due to the dephasing polarization and Doppler broadening. The last term is an oscillation at the intermediate angular frequency ω_{IF} .

B. Experimental results

CP experiments have been performed in order to check the validity of the FID signal model of Eq. (20) in the case of a thermalized sample ($W(0) = W_{\text{eq}}$). We recorded the FID signal of the OCS molecule around 206.745 GHz corresponding to the rotational transition $J = 17 \rightarrow 16$. For a given pressure (i.e., T_2 fixed) and a given relative position r_0 , we measured the FID signal for different pulse durations T_c . After a fast Fourier transform, the amplitude at the intermediate frequency ω_{IF} is proportional to

$$F(\omega = \omega_{\text{IF}}, T_c) = N\sqrt{\frac{T_c}{\Delta\omega}}e^{-\frac{T_c}{T_2}(1-r_0)}. \quad (21)$$

These amplitudes $F(\omega = \omega_{\text{IF}}, T_c)$ measured for different T_c values have been compared with two models. The simplest is given by

$$BP\sqrt{\frac{T_c}{\Delta\omega}}\exp[-T_c(1-r_0)2\pi\gamma_{\text{OCS}}P], \quad (22)$$

which is $|\xi_{\text{app}}^{(1)}(T_c)|$ from Eq. (21) reformulated with experimental parameters. In the second model, the polarization used in Eq. (18) is given by Eq. (9) rather than Eq. (17), corresponding to $|\xi^{(1)}(T_c)|$. The number of molecules N is assumed to be proportional to the gas pressure P , and $T_2 = \frac{1}{2\pi\gamma_{\text{OCS}}P}$ is determined by the OCS self-pressure broadening coefficient $\gamma_{\text{OCS}} = 4.8 \text{ GHz/atm}$ of the $J = 17 \leftarrow 16$ transition, measured in Ref. [22]. The parameter B corresponds to the instrument sensitivity of a given experimental configuration. It accounts for variations in mixer conversion losses and amplifier gains. The value of B is constant for a given experimental configuration. This parameter and the pressure

are fitted against the experimental data sets in the second model. These two values are also used to plot the black curve corresponding to the simplest model. Figure 2 superposes the experimental data (points) with the fitted model $|\xi_{\text{app}}^{(1)}(T_c)|$ from Eq. (22) (black curves) and the model corresponding to $|\xi^{(1)}(T_c)|$ [green (gray) curves]. A good agreement between the experimental and the fitted data is observed for the three different line positions r_0 at $P = 100 \mu\text{bar}$ (corresponding to $T_1 \approx T_2 = 0.3 \mu\text{s}$) and $\Delta\nu = 1000 \text{ MHz}$. For all experimental curves, the relative difference between measured and fitted amplitudes with the simplest model never exceeds 30%. Such differences, especially around $T_c \approx T_{c,\text{max}}$ for $r_0 = 0.1$ and 0.5 , are attributed to the oscillations mentioned above in Sec. II C and seen again on the green (gray) curves. For $r_0 = 0.9$ the oscillations are present over the entire T_c range. Oscillations have also been discussed as “edge effects” by Park and Field [23] for short pulse durations due to the “windowing” of the perturbing electric field. This effect is reduced in our experiment by programming raised cosine edges (5-ns rise time) rather than a rectangular time window in the arbitrary wave generator. The edge effects might explain the underestimated amplitude of the oscillations, given by our model [green (gray) curves], visible for $r_0 = 0.5$ at low T_c values. The signal does not fall to zero for large T_c values, which is consistent with Fig. 1, where the first approximation coincides exactly with the numerical simulation for $\Delta\nu = 1000 \text{ MHz}$. The amplitude of the experimental data in this region is nonetheless higher than that of the fitted curve. This might suggest a shortcoming in the isolated two-level model itself as we can see in Fig. 5 of Hindle *et al.* [5], where other transitions with noticeable intensities around the ground-state (GS) rotational transition $J = 17 \rightarrow 16$ exist in the frequency range covered by the CP [24]. In particular, the intensity of the transition $J = 17 \rightarrow 16$ at 206.966 GHz in the $v_2 = 1$ bending state is only ten times weaker than the GS counterpart at 206.745 GHz. Our hypothesis is that this second transition is polarized by the CP and produces a FID signal at its own frequency. This FID signal at 206.966 GHz may then polarize again the GS transition at 206.745 GHz.

However, the results exhibited in Fig. 2 demonstrate that our simplest model with its approximations is sufficient to reproduce the behavior of the emitted intensities in the chirped-pulse experiment. This conclusion is supported by the analyses of experimental data at $P = 20 \mu\text{bar}$ and $P = 50 \mu\text{bar}$ which show strictly identical patterns.

C. Discussion

1. Optimization of the CP parameters at a given pressure

Equation (20) in the case of a thermalized sample is relatively simple but depends on the parameters T_c , r_0 , T_2 , and N . The signal amplitude at $t' = 0$ can be rewritten in the form of Eq. (22) to show the influence of the gas pressure or equivalently in the following form to show the influence of T_c/T_2 :

$$S_{T_c/T_2}^{r_0} \propto \frac{1}{\sqrt{T_2 \Delta\omega}} \sqrt{\frac{T_c}{T_2}} e^{-\frac{T_c}{T_2}(1-r_0)}. \quad (23)$$

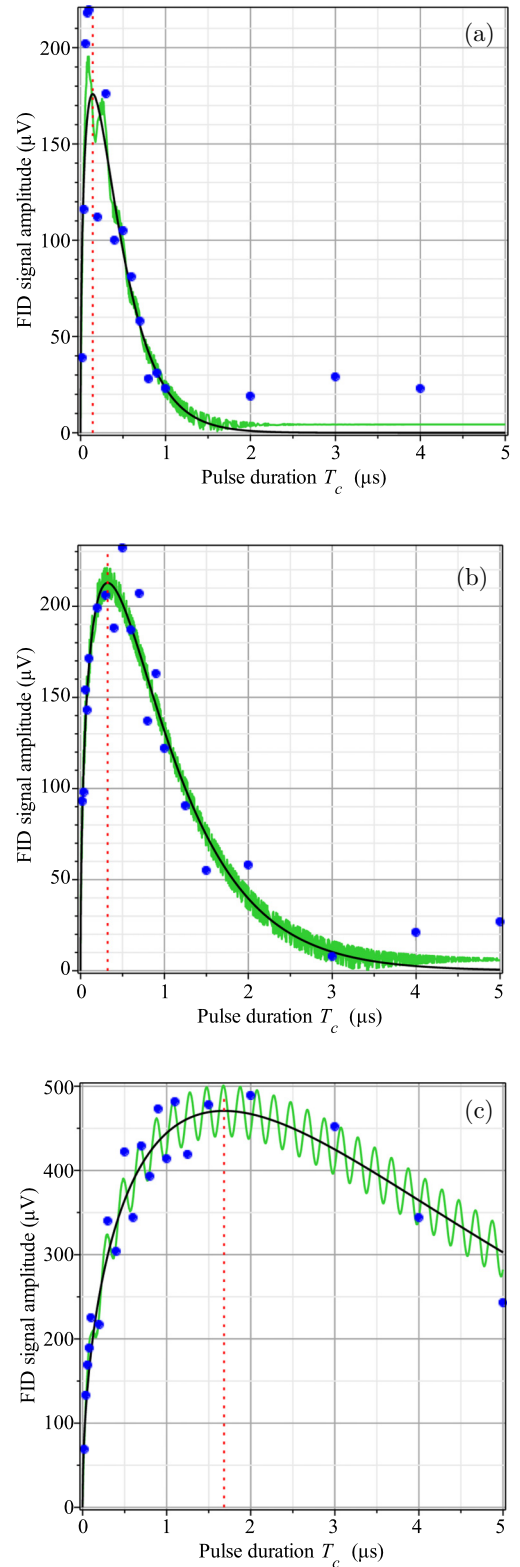


FIG. 2. Comparison between experiment and models, the line position r_0 as a parameter, $P = 100 \mu\text{bar}$, and $\Delta\nu = 1000 \text{ MHz}$. Points are experimental data and the black curve is the fit using Eq. (22) giving $|\xi_{\text{app}}^{(1)}(T_c)|$. The green (gray) curve is a fit where the polarization used in Eq. (18) is given by Eq. (9) rather than Eq. (17) giving $|\xi^{(1)}(T_c)|$. The vertical dotted lines indicate the positions of $T_{c,\text{max}}$. (a) $r_0 = 0.1$. (b) $r_0 = 0.5$. (c) $r_0 = 0.9$.

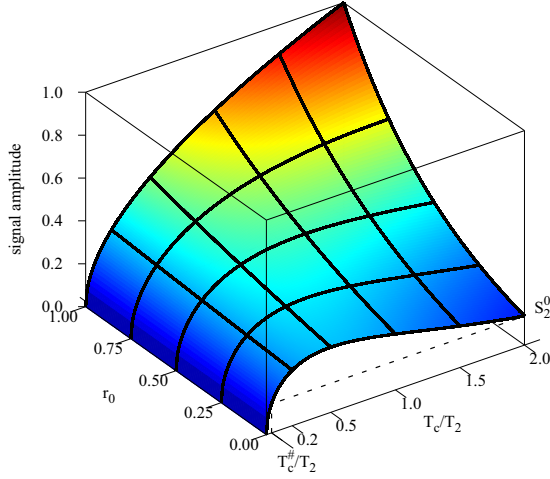


FIG. 3. Three-dimensional view of the amplitude of the signal S in arbitrary units from Eq. (23) versus T_c/T_2 and r_0 at T_2 fixed. $\frac{T_c^{\#}}{T_2} \approx 0.04$ is the solution of the equation $S_{T_c/T_2}^0 = S_2^0$.

Experimentally, T_2 (adjusted with the gas pressure) is fixed by considerations of Fourier transform resolution. For a given T_2 , the optimal pulse duration is given by $T_{c,\max} = \frac{T_2}{2(1-r_0)}$. Figure 3 is a three-dimensional view of the amplitude of the signal from Eq. (23) versus T_c/T_2 and r_0 at T_2 fixed. The dashed line gives the signal amplitude of S_2^0 which intersects the surface at $\frac{T_c}{T_2} = \frac{T_c^{\#}}{T_2}$. It shows that, as long as $\frac{T_c}{T_2} < 0.2$, the signal amplitude is quasi independent of the line position r_0 . Inside this region, the output signal is proportional to $\sqrt{T_c/\Delta\omega}$ and corresponds to the approximation of a fast chirped pulse obtained by McGurk *et al.* [9]. Outside this region, the signal amplitude can be increased significantly but at the expense of a dependence on the line position r_0 within the pulse. However, we observe that up to $\frac{T_c}{T_2} = 2$, the amplitude of the signal for $r_0 = 0$ is always greater than the amplitude for $\frac{T_c}{T_2} = \frac{T_c^{\#}}{T_2}$. In other words, working at $T_c/T_2 = 2$ is more interesting than $\frac{T_c}{T_2} \leq 0.04$ in terms of the signal-to-noise ratio: the gain in amplitude for $r_0 = 1$ is an order of magnitude while the gain for $r_0 = 0$ is at least 1.

2. Dependence of the line strength on the line position

Abeysekera *et al.* [8] experimentally discovered the line position effect on the line intensity. They considered two related experiments to mitigate the problem: in the first experiment, the frequencies were swept to higher values, whereas the frequencies were swept to lower values in the second experiment. They proposed to average the two CP spectra to compensate for the line position effect: $S_{\text{ave}} = (S_{\text{up}} + S_{\text{down}})/2$. They worked with a uniform supersonic flow for which Eq. (23) applies.

The signals are the same in the two experiments except that r_0 in the first one is replaced by $1 - r_0$ in the second one. The corresponding signals are respectively $S_{\text{up}} = A e^{-\frac{T_c}{T_2}(1-r_0)}$ and $S_{\text{down}} = A e^{-\frac{T_c}{T_2}r_0}$, where A is a proportionality constant. The

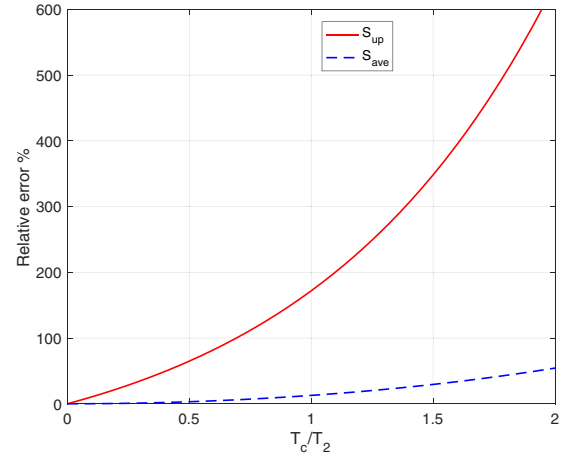


FIG. 4. Relative errors in percent for S_{up} (solid curve) and S_{ave} (dashed curve) as a function of the reduced pulse duration $\frac{T_c}{T_2}$.

average of the two signals is given by

$$S_{\text{ave}} = A e^{-\frac{T_c}{2T_2}} \cosh \left[\frac{T_c}{T_2} \left(r_0 - \frac{1}{2} \right) \right]. \quad (24)$$

In order to estimate the dependence of the FID signal with respect to the line position in the CP, r_0 , we define the maximal relative error for a given T_c/T_2 as

$$\delta_S \left(\frac{T_c}{T_2} \right) = \frac{\max_{r_0 \in [0,1]} S \left(\frac{T_c}{T_2}, r_0 \right) - \min_{r_0 \in [0,1]} S \left(\frac{T_c}{T_2}, r_0 \right)}{\min_{r_0 \in [0,1]} S \left(\frac{T_c}{T_2}, r_0 \right)}, \quad (25)$$

where S is either S_{up} or S_{ave} . A maximum of the two functions is found at $r_0 = 1$, whereas the minimum is found at 0 and $\frac{1}{2}$ for, respectively, S_{up} and S_{ave} . Under these conditions, $\delta_{S_{\text{up}}} \left(\frac{T_c}{T_2} \right)$ and $\delta_{S_{\text{ave}}} \left(\frac{T_c}{T_2} \right)$ are given by

$$\delta_{S_{\text{up}}} \left(\frac{T_c}{T_2} \right) = e^{\frac{T_c}{T_2}} - 1, \quad (26)$$

$$\delta_{S_{\text{ave}}} \left(\frac{T_c}{T_2} \right) = 2 \sinh^2 \frac{T_c}{4T_2}. \quad (27)$$

The plot of these two relative errors as a function of $\frac{T_c}{T_2}$, given in Fig. 4, shows that the heuristic approach of averaging, proposed by Abeysekera *et al.* [8], drastically reduces the effect of the line position on the line intensity. The error $\delta_{S_{\text{ave}}} \left(\frac{T_c}{T_2} \right)$ is lower than 12.5% if $T_c/T_2 \leq 1$ and it is reasonable to use the average spectrum as data for the relative transition intensities. Conversely, if $T_c/T_2 > 1$, the relative error is not acceptable anymore. We then recommend to use S_{up} to correct for the dependence of the line position on the line intensity.

IV. CONCLUSION

The FID signal of a two-level system interacting with a linear CP depends on the polarization at the end of the CP. The value of this polarization, in either thermalized cases (cell or uniform supersonic flow) or nonthermalized cases (molecular beam), was approached through three consecutive analytical approximations which improve the model proposed

by McGurk *et al.* [9]. In particular, the last approximation neglected the oscillations in the polarization and a very simple formula for the optimal pulse duration (for which the modulus of the polarization is maximum) was obtained.

The simple expression between the pulse duration, the line position in the CP, and the signal amplitude will certainly be useful in spectroscopy, where it is convenient to use slower CPs to increase the signal over a fast CP. Moreover, this relation describing the connection between the position of the lines in the CP and their intensity will allow for a correction of the intensities required for high-resolution molecular spectroscopic studies.

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APPENDIX A: DOPPLER BROADENING IN THE FREE INDUCTION DECAY

The FID corresponds to the extinction of the source at $t = T_c$ and the re-emission of the polarized molecules which freely evolve. We perform a change of variable in this section: $t' = t - T_c$.

1. System evolution

Since the source is switched off, the Rabi frequency is set to zero and the optical Bloch equations in the rotating frame [13,25] reduce to

$$\begin{aligned}\frac{dU}{dt}(t') &= -\gamma_2 U(t') - \delta V(t'), \\ \frac{dV}{dt}(t') &= -\gamma_2 V(t') + \delta U(t'), \\ \frac{dW}{dt}(t') &= -\gamma_1 [W(t') - W_{eq}],\end{aligned}\quad (\text{A1})$$

where δ is the detuning from the resonance, null if the inhomogeneous broadening is negligible, and W_{eq} is the population difference at the thermal equilibrium. (U, V, W) is the Bloch vector and the polarization is $\mathcal{P}(t') = [U(t') - iV(t')]N\mu_{ab}$. This is a simple coupled system of differential equations. The third equation is directly integrable, giving

$$W(t') = [W(T_c) - W_{eq}]e^{-\gamma_1 t'} + W_{eq}, \quad (\text{A2})$$

where $W(T_c) = W(t' = 0)$. The remaining part of the system is then

$$\begin{aligned}\frac{dU}{dt}(t') &= -\gamma_2 U(t') - \delta V(t'), \\ \frac{dV}{dt}(t') &= -\gamma_2 V(t') + \delta U(t'),\end{aligned}\quad (\text{A3})$$

which may be diagonalizable to find eigenvalues and eigenvectors and finally the solution:

$$\Rightarrow \begin{bmatrix} U(t') \\ V(t') \end{bmatrix} = \begin{bmatrix} e^{-\frac{\gamma_2}{2}t'} [\cos(\delta t')U_0 - V_0 \sin(\delta t')] \\ e^{-\frac{\gamma_2}{2}t'} [\sin(\delta t')U_0 + V_0 \cos(\delta t')] \end{bmatrix}, \quad (\text{A4})$$

where $U_0 = U(t' = 0)$ and $V_0 = V(t' = 0)$.

2. Inhomogeneous broadening

We must take into account all the contributions due to inhomogeneous broadening characterized by $\Delta\omega_D$, the half width at half maximum, given by

$$\Delta\omega_D = \frac{\omega_0}{c} \sqrt{\frac{2RT \ln 2}{M}}, \quad (\text{A5})$$

where T is the temperature and M is the molecular weight. Different molecules have different frequency resonances due to the Doppler effect and thus different detuning δ . The polarization is given by the integral of Eq. (A4) over all the detunings:

$$\begin{aligned}\begin{bmatrix} U(t') \\ V(t') \end{bmatrix} &= \begin{bmatrix} \int_{-\infty}^{+\infty} e^{-\frac{\gamma_2}{2}t'} [\cos(\delta t')U_0 - V_0 \sin(\delta t')] \sqrt{\frac{\ln 2}{\pi}} e^{-\frac{\delta^2}{\Delta\omega_D^2}} d\delta \\ \int_{-\infty}^{+\infty} e^{-\frac{\gamma_2}{2}t'} [\sin(\delta t')U_0 + V_0 \cos(\delta t')] \sqrt{\frac{\ln 2}{\pi}} e^{-\frac{\delta^2}{\Delta\omega_D^2}} d\delta \end{bmatrix}.\end{aligned}\quad (\text{A6})$$

These integrals are tabulated or can be computed with MAPLE [16], giving

$$\begin{bmatrix} U(t') \\ V(t') \end{bmatrix} = e^{-\frac{\gamma_2}{2}t'} e^{-\frac{\gamma_2^2 \Delta\omega_D^2}{4 \ln 2} t'^2} \begin{bmatrix} U_0 \\ V_0 \end{bmatrix}. \quad (\text{A7})$$

APPENDIX B: DETECTION OF THE FID SIGNAL

In a CP experiment we are interested in the electric field re-emitted during the FID sequence with the polarization given by Eq. (A7). We calculate the electric field in the slowly varying amplitude and phase (SVAP) approximation [9,13]. The general forms for the electric field and the polarization that propagate along the y axis are

$$E(y, t') = \frac{1}{2} [E_r(y, t') + iE_i(y, t')] e^{-i(\omega_0 t' - ky)} + \text{c.c.}, \quad (\text{B1})$$

$$P(y, t') = \frac{1}{2} N\mu_{ab} [U(t') - iV(t')] e^{-i(\omega_0 t' - ky)} + \text{c.c.} \quad (\text{B2})$$

The SVAP approximation neglects the amplitude and phase variations during temporal and spatial periods:

$$\frac{\partial E}{\partial y} \ll kE, \quad \frac{\partial E}{\partial t'} \ll \omega E, \quad \frac{\partial P}{\partial t'} \ll \omega P.$$

If we neglect also $\frac{1}{c} \frac{\partial E}{\partial t'}$ compared to $\frac{\partial E}{\partial y}$, we get simplified propagation equations for the real and imaginary parts:

$$\frac{\partial E_r}{\partial y} = \frac{k}{2\varepsilon} N\mu_{ab} V, \quad (\text{B3})$$

$$\frac{\partial E_i}{\partial y} = \frac{k}{2\varepsilon} N\mu_{ab} U, \quad (\text{B4})$$

equations that we can easily integrate between $y = 0$ and $y = L$ corresponding to the length of the gas cell:

$$E(L, t') = \frac{k}{4\epsilon} N \mu_{ab} L (V + iU) e^{-i(\omega_0 t' + \Phi)} + \text{c.c.}.$$

Finally, taking Eq. (A7) into account, we get

$$E(L, t') = \frac{k}{4\epsilon} N \mu_{ab} L e^{-\frac{t'}{T_2}} e^{-\frac{t'^2 \Delta\omega_D^2}{4 \ln 2}} \sqrt{U_0^2 + V_0^2} \times e^{-i(\omega_0 t' + \Phi - \theta)} + \text{c.c.}, \quad (\text{B5})$$

where $[U_0; V_0] = [U(t = T_c); V(t = T_c)]$.

In the experiment, we access the electric field by a heterodyne scheme tuned in the way to observe $S(t') = A E(t') \cos(\nu_{\text{IF}} t' + \phi)$, where A is a constant depending on mixer efficiency, amplifier gain, etc.; ν_{IF} is the intermediate frequency ($\nu_{\text{IF}} = \nu_0 - \nu_{\text{LO}}$); and ϕ is the phase at the origin of time:

$$S(t') \propto |\mathcal{P}(T_c)| e^{-\frac{t'}{T_2}} e^{-\frac{t'^2 \Delta\omega_D^2}{4 \ln 2}} \cos(\nu_{\text{IF}} t' + \phi). \quad (\text{B6})$$

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