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# 1D SINGLE-SHOT MULTI-SCALAR MEASUREMENTS FOR TURBULENT FLAMES: CO<sub>2</sub> SPONTANEOUS RAMAN SCATTERING

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## Abstract

Whether in-situ measurements of CO<sub>2</sub> are a key point for describing combustion process and its efficiency, yet they still challenging in high temperature reactive flows. This article presents the first steps to validate CO<sub>2</sub> measurements by Spontaneous Raman Scattering (SRS) using a spectral fitting method. Average and instantaneous Raman CO<sub>2</sub> spectra have been processed for number density measurements thanks to a new model for CO<sub>2</sub> SRS simulation at high temperature. Accuracy and uncertainties of CO<sub>2</sub> density number in simplified environment are analysed. These initial results highlight the potential of the SRS simulation fitting based diagnostic for CO<sub>2</sub> measurements in flames.

## 1. Introduction

The deep understanding of combustion phenomena, motivated by both economic and ecological issues, has justified the development of more sophisticated optical diagnostics over the past years. More specifically, theoretical and numerical combustion models need accurate multi-scalar and scalar gradients to be validated. Under this concept, Spontaneous Raman Scattering (SRS) has proven to be a compelling response to multi-scalar measurements needed in flames [1-3].

SRS involves a shift in wavelength of the scattered light which depends directly on the spectroscopic nature of the probed molecules. This so-called "Raman shift" can be used to identify but also quantify them [4]. If most of combustion reactants and products are Raman active, the quite low Signal Noise Ratio (SNR) limits nonetheless accuracy and detectability to the major components in flames (such as CH<sub>4</sub>, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O...).

Two methods are mostly used to calculate number density by SRS. The first is based on calibration procedure and has the advantage to be low resources demanding and to treat easily complex molecule [5]. The other method is based on fitting simulation spectra and thus a thorough knowledge of the probed molecule spectroscopy is required [6]. Due to the complexity of modelling SRS spectra of polyatomic molecules, the calibration method is the mostly used although the associated calibration procedure remains quite cumbersome. Furthermore, a hybrid method [3] also exists and uses the RAMSES library [7] for the simulation part.

CO<sub>2</sub> is a major product of hydrocarbons combustion. Consequently, its in-situ quantification is essential to characterize combustion process. However, CO<sub>2</sub> SRS is ruled by a more complex spectroscopy than for diatomic molecules. Even if a lot of publications [8-10] already described deeply CO<sub>2</sub> energy states, databases for CO<sub>2</sub> at high

temperature such as HITEMP [11] or CDS [12] are unfortunately designed for absorption or emission experiments. Therefore these common spectroscopic databases do not include Raman transition moments, which are however essential to simulate correctly CO<sub>2</sub> Raman spectra [13]. Nevertheless, a new table with a set of CO<sub>2</sub> Raman shifts associated to their polarizability transition moment has been recently released by Lemus et al [14]. These data have been computed for combustion optical diagnostic purposes. The large number of vibrational transitions involved in this model should be acceptable to build quite reliable CO<sub>2</sub> spectra at high temperature. By harnessing this recent table, instantaneous CO<sub>2</sub> density number measurements should be carried out by the spectral fitting method.

## 2. Specific objectives

In the present study, CO<sub>2</sub> Raman transitions from a recent spectroscopic database have been added to the library of CORIA's Raman simulation algorithm [15]. In this way, simulated CO<sub>2</sub> Raman spectra can be built depending on temperature. To validate this CO<sub>2</sub> model, measurements are carried out in simplified environments with the CORIA's experimental Raman setup [16]. Several cases are studied in order to cover a wide range of temperatures and densities (electrically heated flows for low temperature and premixed laminar flame with various equivalence ratios in Bunsen burner for high temperature). CO<sub>2</sub> SRS simulations are carried out from these experimental data, in order to determine CO<sub>2</sub> number density. Accuracy and uncertainty of the average and instantaneous values are discussed.

## 3. Experimental and simulation

### 3.1 Raman experimental setup

One of the distinguish features of SRS signal is its relative weakness, requiring the use of high energy laser excitation associated to appropriate sensitive

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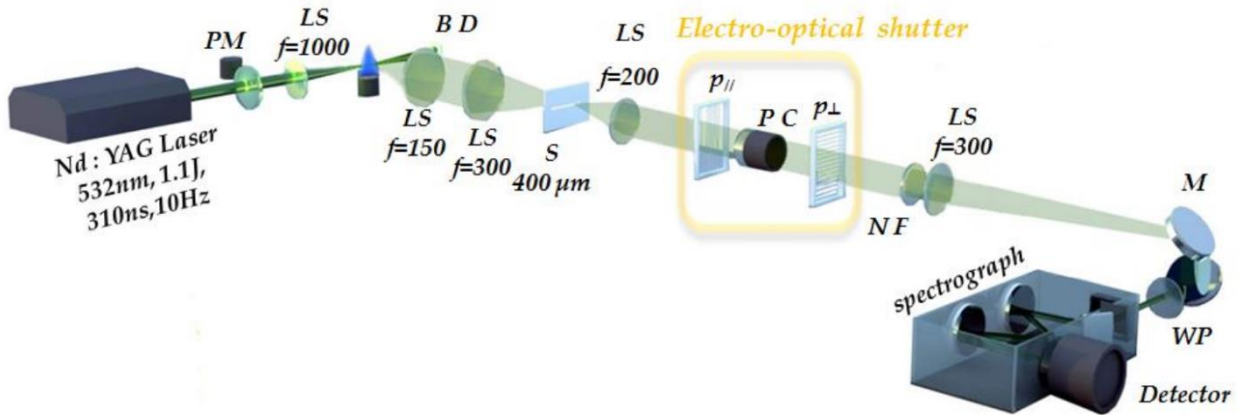


Fig 1 : Overview of the experimental set-up: S, slit; LS, Lens (AR coated @400-700nm) PC, Pockels Cell; P, Polarizer; BD, beam dump; PM, Power meter; NF, Notch filter (532 nm, FWHM 20 nm); WP, Waveplate ( $\lambda/2$ , AR coated @400-700nm)

detection system to reach high spatial and temporal resolution SRS measurements.

Figure 1 provides the overview of the experimental Raman setup. The excitation system consists in a high energy (greater than 1000mJ) laser pulses produced by the second harmonic (532nm) of a Nd:YAG laser (Agilite, Continuum) at 10Hz. The pulse duration is set at 310ns to stay under turbulence time scale and also to avoid optical breakdown due to excessive local irradiance. The laser beam is focused by a long focal-length lens ( $f=1000$  mm) providing an almost constant 170  $\mu\text{m}$ -thick probe volume for several millimetres.

The scattered light from a 3 mm-length probe volume is collected at  $90^\circ$  with a large solid angle by a first telescope of lenses. These latter are achromatic to avoid optical aberrations. Then, a 400 $\mu\text{m}$ -wide slit remove most of the emission from regions away from the probe volume. A second telescope of achromatic lenses and a periscope reimage the horizontal beam image for the 250 $\mu\text{m}$  slit vertical entrance of an imaging spectrograph (SpectraPro 300i, 1200-600g/mm gratings blazed at 500nm,  $f=300\text{mm}$ ,  $f/4$ , Acton Research). An achromatic half-wave plate (AHWP10M-600, Thorlabs) is placed in front of the slit because of the polarization of the spectrograph's grating. Last but not least, a Notch filter (NF03-532E, OD=6 at 532nm, FWHM=17nm, Semrock) is placed in the collimated region of the second telescope. As a matter of fact, Rayleigh and Mie scattering are several orders of magnitude higher than SRS and hence these elastic scattering lights have to be rejected before detection.

A CCD camera completes the imaging spectrograph. In the past, several detection systems have been compared [16] for 1D single-shot measurements by SRS. Full-frame back-illuminated CCD camera (Pixis 400B, 400 x 1340 pixels, Princeton Instruments) appeared to be the most suitable both for its high quantum efficiency (>90%) and his low readout noise (<13e-). Unfortunately, such CCD cameras have no gating system. This may lead to a continuous exposing for the pixels during the readout time and can become a real struggle because of flame emission. For this main reason, a

fast electro-optical shutter has been developed to complete CORIA's experimental Raman setup. This shutter is composed of two crossed polarizers (19WG-50, Quantum Technology) and a Pockels cell (LAP-50, KD\*P, Quantum Technology). An HV generator (HVP-5LP, Quantum Technology) drives the Pockels cell crystal to get a 500 ns gate width. More information and specifications about this original electro-optical shutter can be found elsewhere [17].

### 3.2 CO<sub>2</sub> Raman spectra modeling

Accurate instantaneous temperatures and density number measurements in flames have been obtained for N<sub>2</sub>, O<sub>2</sub> and CO, i.e. diatomic molecule in previous works [16]. This was mainly achieved by an appropriate library and a well-established experimental procedure [18]. To extend measurements to CO<sub>2</sub>, we must first of all complete our library with all the necessary information to build reliable spectra (i.e. energy levels, Raman shifts and line strength). For combustion diagnostic, these data need to be also relevant at high temperature.

For CO<sub>2</sub>, the three vibrational modes (symmetrical and antisymmetrical stretch modes and a double degenerated bend mode) increases the number of vibrational energy levels compared to diatomic molecules. Furthermore, the Fermi resonance that occurs between the bending mode and the symmetrical stretch mode, leads to important perturbations of the energy levels. This implies that the standards expressions [19] used previously for diatomic molecules to calculate energy levels, are no more appropriate to describe CO<sub>2</sub> resonant states. Other interactions also exist [8] (such as Coriolis interaction) and should be taken into account to describe closely the highest energy states. Besides Raman shifts computation, energy levels are also needed to calculate intensity for each transition. For CO<sub>2</sub>, the differential cross section can be expressed for the transition from state  $i$  to state  $f$  as the product of this specific Raman line strength and Boltzmann population distribution as following [13]:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{i\rightarrow f} = \left(\frac{\pi}{\epsilon_0}\right)^2 \frac{(\nu_0 + \nu_i - \nu_f)^4}{Z_{vib}(T)} g_{if} (M_{if})^2 \times \exp\left(\frac{-h\nu_i}{k_b T}\right) \quad (1)$$

$$\Lambda = N_{ref}^{N_2} \frac{\sum_{v,J} \sum_{QSO} f_{v,J}(T_{ref}) \left(\frac{\partial\sigma}{\partial\Omega}\right)_{v,J \rightarrow QSO}^{N_2}}{\int_0^\infty S_{SRS}^{N_2}(\lambda, T_{ref}) d\lambda} \quad (3)$$

With  $\epsilon_0$  the permittivity of vacuum,  $h$  the Planck constant,  $k_b$  the Boltzmann constant,  $\nu_0$  the wavenumber of the exciting radiation,  $\nu_i$  and  $\nu_f$  respectively the initial and final levels involved in the transition,  $g_{if}$  the vibrational degeneracy of the transition, and  $Z_{vib}(T)$  the vibrational partition function. Transition moments  $M_{if}$  are calculated by using approximate expressions derived from the theory of perturbations and values mean polarizability and its derivatives. These latter can be obtained with respect to a basis set of symmetry or normal coordinates from the fit to experimental transition moments [13]. However, an algebraic approach using curvilinear coordinates has been recently used to predict energy levels and transition moments for CO<sub>2</sub> [14]. The simulation of the spectra obtained with this algebraic method showed results close to experimental accuracy [20]. To go further, 892 CO<sub>2</sub> Raman transitions were also computed and their relative data (e.g. energy levels, Raman shift and transition moment) were released specifically for application in combustion diagnostic. These data have been added to the Raman spectroscopy library previously developed [15], assuming that CO<sub>2</sub> transitions were purely vibrational. This hypothesis is justified by the smallness of vibrational-rotational interaction in CO<sub>2</sub> which leads to strong Q-branches that overlap [4], by the high number of nearby vibrational transition of the model combined to the moderate spectral resolution of the setup. The dependence of depolarization was also not taken into account.

Once Raman shifts and intensities for each transition are known, Raman peaks are convoluted with the apparatus function. The latter are obtained in-situ by fitting simulation spectra with measurements in ambient air, using a sum of three Gaussian functions as approximation of the instrumental function. Then absolute temperature is determined by fitting through a minimization procedure the simulated rovibrational spectra of N<sub>2</sub>, whose accurate thermometry in flames had been proved in previous works [16]. CO<sub>2</sub> spectra are then built at this temperature and CO<sub>2</sub> molecular density is obtained from the following equation:

$$N^{CO_2} = \Lambda \frac{\int_0^\infty S_{SRS}^{CO_2}(\lambda, T) d\lambda}{\sum f_{if}(T) \left(\frac{\partial\sigma}{\partial\Omega}\right)_{i\rightarrow f}^{CO_2}} \quad (2)$$

Where  $\Lambda$  is estimated by measurement in ambient air as following:

Laser energy fluctuations for single-shot measurement were also estimated and taken into account simultaneously on the basis of the instantaneous N<sub>2</sub> number density.

Furthermore, we noticed a discrepancy between the absolute values of the differential cross sections of N<sub>2</sub> and CO<sub>2</sub>, which do not rely on the same library. As performed in [6], a correction coefficient was determined experimentally with Raman spectra of CO<sub>2</sub> and N<sub>2</sub> at ambient temperature, this coefficient increases the CO<sub>2</sub> cross section by a factor 1.315.

#### 4. Results and Discussion

In this section, the validity of this new CO<sub>2</sub> Raman model is analyzed. Since our method is only based on spectra simulation, potential discrepancies between synthetic and experimental spectra may affect in the end the accuracy of measurements. Several cases of experiments were looked at to compare simulated spectra to experimental. These simple cases were selected to cover the wide range of temperatures and CO<sub>2</sub> densities one could meet in combustion environment. The first measurements of number density obtained with this model are also shown and discussed.

##### 4.1 Number density in controlled heated flows

To make CO<sub>2</sub> SRS measurements at low temperature, cold gases were heated using an 8kW electrical heater (Sureheat JET, OSRAM Sylvania). The target temperature was reached thanks to a control loop using a K-type thermocouple at the outlet of the heater. The maximum temperatures extended to about 1000K. Several CO<sub>2</sub>/Air ratios, provided by RMS flowmeters were thus heated. Flow rates were always above 60slpm to avoid the overheating of equipment. The heater was placed vertically and the measurements were made to the closest position from the exit to avoid dilution with ambient air.

A comparison of simulated spectra and experimental data is shown in figure 2. The dots represent the average spectrum (400 spectra) of pure CO<sub>2</sub> heated at 1000K. The red line is the synthetic spectrum built at 1000K and was fitted in term of experimental wavelength shift and intensity.

The simulated spectrum is quite similar to the experimental one. The two specific parts of CO<sub>2</sub> Raman spectra are quite well reproduced by the model in respect of their relative intensities and positions. This can be seen on the low values of residuals (green line) that are globally below 10%.

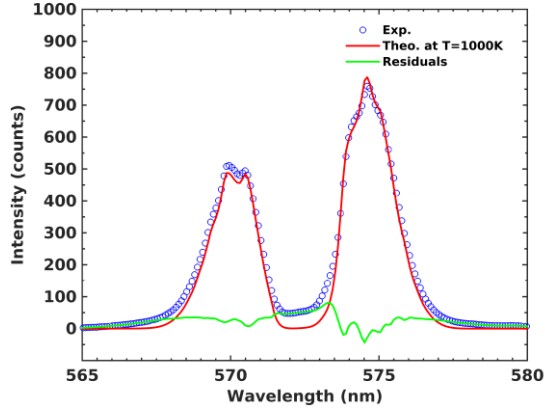


Fig. 2: Average  $\text{CO}_2$  spectra acquired in heated flow (pure  $\text{CO}_2$ ) with  $300\mu\text{m}$  spatial at  $T=1000\text{K}$

Nevertheless, the part between the two main simulated peaks shows a noticeable difference with the experimental data. While the simulation returns to zero in this region, the experimental spectrum shows a quite constant shift between the two main profiles. This particularity has also been found on most of the experimental spectra. It is important to note that no vibrational transition appears in our database for this range of wavelength. Since widening the instrument function actually showed a quite insignificant impact to bridge the gap between simulation and experiments in this part of the spectra, this raised signal is assumed to be some marks of rovibrational Raman transitions occurring in this range of wavelength. This might be considered a limit for our model since only vibrational transitions were taken into account. Anyway,  $\text{CO}_2$  number density measurements have been carried out to see if this little discrepancy has a significant effect on the accuracy.

A mixture of 25%  $\text{CO}_2$  and 75% air is heated from 550K to 1000K with steps of 50K. The average experimental SRS signals are displayed in figure 3. The two parts of the  $\text{CO}_2$  SRS spectra are easily identifiable near 571 and 574nm. The “shift” part mentioned previously is also recognizable between 572nm and 573nm. The signal close to 579nm is related to the  $\text{O}_2$  SRS. The first effect of the rise in temperature is a general decrease of the SRS signal, mainly due to the dilatation of the gases in the probed volume. Beside this signal reduction, spectra are also distorting with temperature increasing. For example, it can be seen that the initially maximum intensities at 571nm and 574nm of  $\text{CO}_2$  SRS signal progressively declines with temperature to finally be lower than the peaks at 570nm and 575nm. This behavior corresponds in fact to the growing population of first excited energy states at the expense of the ground level. This thermal dependence shows also the potential of study of  $\text{CO}_2$  SRS for temperature measurements.

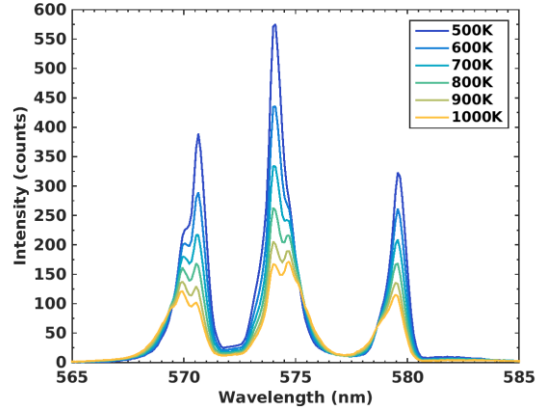


Fig. 3: 400-shot averaged spectra acquired in heated flow (25% $\text{CO}_2$  75%Air) with  $300\mu\text{m}$  spatial resolution at different temperatures

Since the prior objectives are to make number density measurements, temperature was first deduced from  $\text{N}_2$  SRS average signal with a procedure presented in a previous work [18], to build  $\text{CO}_2$  synthetic spectra at the measured temperature. The fidelity of simulated spectra with experimental spectra lets envisage to measure temperature from  $\text{CO}_2$  spectrum fitting. Then the number density is determined by fitting average experimental  $\text{CO}_2$  spectra and from eq. 2 and 3, with the temperature determined by fitting the  $\text{N}_2$  SRS spectrum. Average calculated number densities are plotted against temperature in figure 4. The theoretical number density, following the ideal gas law, is also shown. Same orders of magnitude have been found between the compared quantities with accuracy of 3,5% and below, and the hyperbolic behavior is well reproduced.

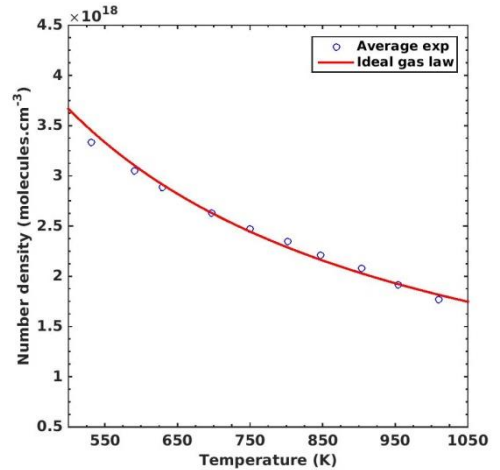


Fig. 4: Scatter plots of average  $\text{CO}_2$  number density measurements versus temperature in a heated flow

Instantaneous spectra were also processed by our algorithm, using the same experimental data and procedure. An example of simulated spectra get from instantaneous measurements is shown in figure 5. We can notice that the simulation remains quite reliable for single-shot data at low temperatures.

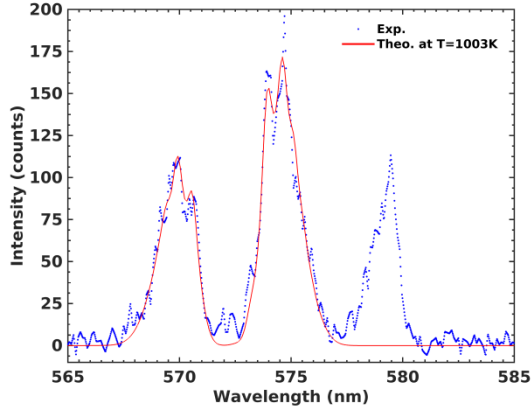


Fig. 5: Single-shot  $\text{CO}_2$  and  $\text{O}_2$  spectra acquired in an heated flow (25% $\text{CO}_2$  75%Air) with  $300\mu\text{m}$  spatial at  $T=1000\text{K}$

Instantaneous number density measurements for ten operating points (400 single shots each) are compiled and displayed in figure 6.

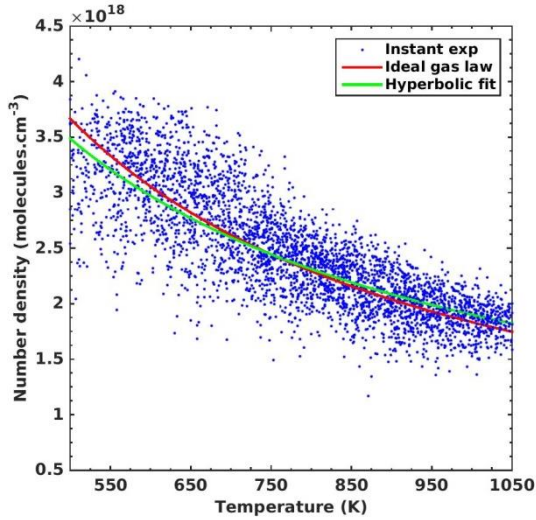


Fig. 6: Scatter plots of instantaneous  $\text{CO}_2$  number density measurements versus temperature in heated flows

As for the average values, instantaneous number densities have close values to the theoretical ones and the hyperbolic behavior is always quite well reproduced as can be seen with the hyperbolic fitting. Single-shot measurements induced nonetheless a moderate dispersion of the values leading to less than 10% of uncertainties over this range of temperature.

#### 4.2 Number density in premixed laminar flame

$\text{CO}_2$  SRS measurements at high temperature are performed in a Bunsen burner fed with a methane-air mixture with equivalence ratio of  $\Phi=1$ . Air and fuel flowrates are controlled by sonic nozzles. Measurements were performed 24 mm above the burner, i.e. in the burnt gas areas of the flame. In previous works [18] this region showed homogenous temperature and composition, quite close to equilibrium conditions. Instantaneous  $\text{CO}_2$  molar

fractions are displayed and compared with the equilibrium value obtained from GASEQ [21] in figure 7.

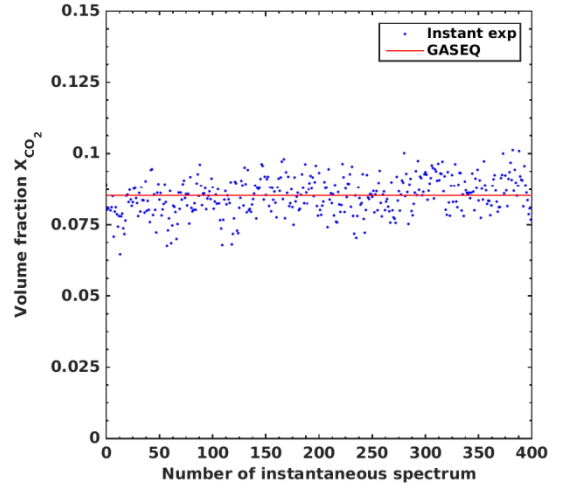


Fig. 7: 400 instantaneous  $\text{CO}_2$  number density measurements in burnt gases with  $300\mu\text{m}$  spatial resolution

Volume fractions have close values to the equilibrium composition. A high accuracy (below 1%) is noticed for this operating point. Uncertainties are not greater (7,5%) than for the case at low temperature despite the drop of SNR at high temperature. As a matter of fact,  $\text{CO}_2$  spectra simulated at  $T_{N_2}$  looks quite reliable, as can be shown in figure 8.

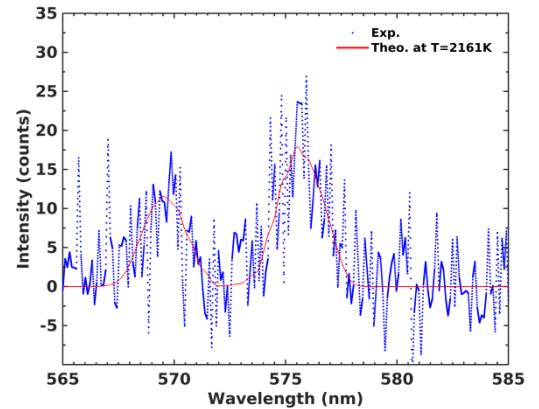


Fig. 8: Single-shot  $\text{CO}_2$  Raman spectra acquired in stoichiometric methane-air flame with  $300\mu\text{m}$  spatial resolution

However, other equivalence ratios will be investigated in the future to see if this good accuracy and these moderate uncertainties are almost constant for other operating points.

## 5. Conclusion

The first results presented in the paper show that the new theoretical model is reliable for  $\text{CO}_2$  SRS simulation at low and high temperatures despite the hypothesis of pure vibrational transition. Synthetic spectra were built and showed results close to

experimental for a wide range of temperature and density. Average and instantaneous CO<sub>2</sub> number densities have been measured with high accuracy (more than 96%) in hot gases and in a laminar stoichiometric flame. Analysis of spectra and measurements at other operating points will continue to develop an appropriate experimental procedure to further reduce uncertainties. Furthermore, forthcoming SRS measurements in lean flame will also take advantage of the high potential of the spectra fitting method compared to the calibration or hybrid method by solving the issue of the overlapping between CO<sub>2</sub> and O<sub>2</sub> SRS signal. With our experimental setup and our SRS post-processing procedure [15] CO<sub>2</sub> spectra can be considered to measure the absolute instantaneous temperature.

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