ADVANCEMENT OF COHERENT ANTI-STOKES RAMAN SCATTERING SPECTROSCOPY FOR APPLIED MEASUREMENTS IN COMBUSTION AND HIGH SPEED FLOW ENVIRONMENTS

by

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Dedicated to my parents, whose support has been the foundation of everything

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ABBREVIATIONS

CARS	Coherent Anti-Stokes Raman Scattering
ERE-CARS	Electronic Resonance Enhanced CARS
WIDECARS	Width-increased dual-pump enhanced CARS
V-CARS	Vibrational CARS
R-CARS	Rotational CARS
LIF	Laser Induced Fluorescence
PLIF	Planar Laser Induced Fluorescence
ns	Nanosecond
\mathbf{ps}	Picosecond
fs	Femtosecond
NRB	Non-resonant background
$\rm CH_2O$	Formaldehyde
OPG	Optical Parametric Generation
OPA	Optical Parametric Amplification
LBO	Lithium Triborate
BBO	Beta Barium Borate
NRB	Nonresonant background
kHz	kilo-Hertz
FTIR	Fourier Transform Infrared
PLEET	Picosecond Laser Electronic Excitation Tagging
FLEET	Femtosecond Laser Electronic Excitation Tagging
HST	High Temperature Shock-Tube at Sandia National Laboratories
RDE	Rotating detonation engine

ABSTRACT

Laser diagnostic techniques are a powerful tool for the understanding of multiphase dynamic environments related to the development of energetic materials [1]–[3], aeronautical and space propulsion systems, and novel high energy shock physics [4], [5]. In particular, Coherent Anti-Stokes Raman Scattering (CARS), first applied in 1973 [6] has been employed for high fidelity measurements of temperature[7], concentration[8]–[10] and pressure [11] for novel combustion environments [12] such as high pressure burners [13], pool fires[14], and rotating detonation engines (RDE)[15].

The current work focuses on (i) advancing the sensitivity of CARS for minor species concentration measurements, and (ii) advancing the repetition rate of CARS temperature measurements from the 100s Hz to 100s kHz for flame conditions and real-world applications such as high enthalpy shock tubes and blasts.

In part (i) quantitative nanosecond electronic resonance enhanced Coherent Anti-Stokes Raman Scattering spectroscopy (ERE-CARS) is presented for for the measurement of formaldehyde (CH_2O) concentrations in reacting and non-reacting conditions. The three-color scheme utilizes an electronically resonant probe which allows detection of CH_2O at concentrations as low as 9×10^{14} molecules/ cm^3 (55 parts per million) in a calibration cell with CH_2O and N_2 with a maximum of 3% uncertainty. The pressure dependence is studied up to 11 bar, and the technique further applied to characterize the CH_2O concentration in an atmospheric premixed dimethyl ether/air McKenna Burner flame, with a maximum concentration uncertainty of 11%.

(ii)A burst-mode nitrogen (N_2) picosecond vibrational coherent anti-Stokes Raman scattering (ps-VCARS) system is presented for accurate flame thermometry at 100 kHz repetition rate. A frequency-tripled ps burst-mode laser is used to pump a custom optical parametric generator/amplifier (OPG/OPA) to produce 607 nm broadband Stokes pulses with 120 cm^{-1} bandwidth, along with a narrow-band 532 nm pump/probe beam. A novel simultaneous shot-to-shot nonresonant background (NRB) measurement is implemented to account for Stokes spectral profile and beam overlap fluctuations. The 100-kHz ps-VCARS data are bench-marked in a near-adiabatic CH_4 /air Hencken calibration flame with an accuracy of 1.5% and precision of 4.7% up to peak flame temperatures. The use of N_2 VCARS and simultaneous NRB measurements enables accurate high-speed thermometry for a wide range of fuels and combustion applications.

The developed burst-mode ps-VCARS system described above was applied first to a turbulent jet flame, and then to a fireball environment in parallel with pyrometry temperature measurements to simultaneously determine the gas and the particle phase. Results from nitrocellulose and from black powder fireballs are shown.

The system was also employed to further the understanding of the physics occurring in a high enthalpy shock tube at Sandia National Laboratories. Here, the 100 kHz measurement allowed to measure the pre-shock, incident and reflected shock conditions at temperatures between 300K and \sim 5,000 K.

Furthermore, it was found that development of an accurate model for picosecond CARS was needed to accurately analyze the data. For this, a novel approach is presented to model the pump and stokes pulses as a summation of time delayed impulse response functions, which are probed by an appropriately placed probe pulse, and then incoherently summed over the time interval of interest. This model enables to improve the accuracy of the spectral fitting, and hence the temperature accuracy of the measurement technique. Extensive validation and comparison to other CARS models is shown to explain the space of validity of the model.

The combination of a developed burst-mode system, a single shot nonresonant bandwidth referencing technique, and a physically accurate fitting model have made it possible to put together an instrument to reliably perform measurements in various field environments at temperatures from 700 to >4,000 K with an uncertainty of 4.8%.

Finally, improvements to the ps-CARS model, future work and other possible laser architectures are discussed.

1. INTRODUCTION

1.1 Motivation

The purpose of this dissertation is to highlight the progress which has been made in the advancement of Coherent Anti-Stokes Rama Scattering spectroscopy (CARS) to being a more applied and reliable technique for dynamic and large scale environments for combustion and hypersonic flows. The new measurement of CH_2O as a minor species [16] adds the ability to track minor species such as CH_2O and other pollutants in combustion. This is important because CH_2O is a key intermediate in multiple concurrent reactions, and measuring CH_2O as well as other major species, with WIDECARS, for example [17], modelers can test and improve their chemical kinetics simulations. The measurement is also shown to be effective in high pressure environments, and could be applied to high pressure burners, or internal combustion engines[18]. A significant part of the work on CH_2O was focused also on characterizing unexpected spectral features resulting from the ERE-CARS technique. As a key aspect for developed techniques is also to ensure that they can be repeatable used in the field, improvements on the stability of the already established WIDECARS measurement technique for multi-species detection, are shown.

On the other hand, a major development of CARS is presented in the extension to high repetition rate measurements in relevant environments. A solid state burst-mode pumped picosecond vibrational Nitrogen CARS system was developed and then bench-marked in adiabatic flames, the repeatability and accuracy of the system were improved through the implementation of concurrent nonresonant background corrections on a shot-to shot basis[19]. Subsequently, the CARS system, of which three were built by the author, was used to perform measurements in a variety of challenging environments: turbulent flames and jets, in energetic materials fireballs [20], and in a hypersonic shock tube. These applications show extensive use of the 100 kHz ps-CARS in relevant environments is feasible and already ongoing. Due to the uniqueness of the picosecond time-scale being on the order of the Raman coherence decay time, there was lack of appropriate modeling for ps-CARS regime. After testing various approaches, a novel incoherent sum method was created and demonstrated to be physically and mathematically accurate to perform the data fitting. This modeling was used throughout for the data fitting, and is described and validated thoroughly in a later chapter. Finally, the potential of extending the 100 kHz measurements and the advancements necessary for measurements at \sim 300kHz-1 MHz are discussed, as well as additional options and steps to be taken to improve the accuracy and stability of the measurement.

1.2 CARS overview and background

1.2.1 purpose of CARS in combustion

In recent years the advent and development in hypersonic flight technologies has required new experiments and modeling to understand the complex physics occurring due to conductive, convective and radiative heat transfer. The first working laser was demonstrated by T.H. Haiman in 1960 [21]. In the first ~ 10 years of its existence, the LASER was used extensively for combustion experiments, as is detailed by the following review article published in Combustion and Flame in 1969, which referenced > 400 publications, many of which concerned laser diagnostics in combustion [22].

Since the 1970s [8], [23]–[27] understanding of combustion and flow environments has been highly dependent upon the use of laser diagnostics to qualitatively characterize the flow and particle speed, as well as the temperature and chemical species presence and distribution, in one[4], [28], [29],two[30]–[33], and three[34]–[36] dimensions. While many techniques have been invented and used only a handful of times. Some of the ones which have persisted and are most commonly used can be divided by the measurements they provide, the following is a non-exhaustive list of these, with a couple referenced applications. For fluid flow velocities: Particle Image Velocimetry and its variants[37], as well as Doppler laser velocimetry, and Rayleigh scattering[25], [31], [32]. For flame fronts and shock waves enhanced visualization and some concentration measurements Schlieren [36], [38] and Laser induced fluorescence have been widely used[39], with LIF also being applied to qualitative measurement of species and, in some cases, temperature measurements (in 1,2,3 dimensions)[18], [30], [39]–[45]. Species concentrations and temperature have been determined using Rayleigh Scattering[25], [31], [32], Raman Scattering[24], [29], Absorption spectroscopy[46]–[48], and CARS[12], [49]–[52]. Among the described techniques, CARS was first explored in 1965 by Maker et al. [53]. CARS has been widely adopted for gaseous concentration and temperature measurements in combustion and high speed flows, with a few recent uses to measure pressure. The adoption of CARS is not random, there are many advantages to it, especially at flame temperatures. Overall, it can provide absolute measurements of concentration and temperature on a single-shot basis, it has the unique features of providing measurements from a single point $(\sim 100 \times 100 \times 500 \mu m)$, of a laser-like output which can be arbitrarily propagated to get rid of the characteristically strong background emission from most combustion environments; and finally, especially important is the fact that the signal is at a shorter wavelength than the laser pulses, spectrally separating it from the many processes (Raman Scattering, four wave mixing, Rayleigh scattering, Laser induced fluorescence) which happen at energies equal to, or lower than the excitation pulses. In particular CARS spectroscopy has enabled quantitative measurements of chemical species concentrations, such as Nitrous Oxide 54, [55], OH[49], Indium Iodide[56], some liquid dyes, CH, and acetylene [10], [27], [56]–[61], rotational [62], [63], vibrational [64], [65], and rovibrational temperature [66], and even pressure [67], [68]. Additional references can be found in a 2010 CARS review by Roy et. al[12].

The current advancement in CARS is now focused on four main aspects: 1) Expanding to the detection of additional species, or more species simultaneously;2)Improving the temperature accuracy of the measurement; 3) Increasing the measurement rate of CARS to obtain more information in high-speed flows 4) Increasing the dimensionality of the measurement, to provide more instantaneous information on the flow, This thesis shows progress in the first three areas.

1.2.2 CARS Theory

Coherent Anti-Stokes Raman Scattering Spectroscopy is a four wave mixing process in which two simultaneous pulses of energies ω_1, ω_2 , create a coherence in the molecule of interest, which is then probed by a third pulse of energy ω_3 . The outgoing CARS signal is scattered at $\omega_4 = \omega_1 - \omega_2 + \omega_3$ if a change in polarizability is produced in the molecule. As shown in figure 1.1, $\omega_1, \omega_2, \omega_3$ mix differently. There are different ways that the waves can interact, of which CARS is only one of these; the resonant processes are labelled as CARS, Coherent Stokes Raman Scattering, Stimulated Raman Gain, and Stimulated Raman loss. Fortunately, the detection of these is at different frequencies, and filtering or dispersion through a spectrometer can limit detection to fewer processes, although it should be noted that all of these processes continue to happen even if we are not measuring them.



Figure 1.1. Resonant mixing processes that occur when three frequencies are sent into the probe volume

Selection of the CARS wavelength range will yield measurement of the resonant molecular response, as well as the nonresonant mixing of the beams, as seen in figure 1.2. To obtain nontrivial information, the frequencies are chosen so that $\omega_1 - \omega_2$ corresponds exactly to a resonant transition of the molecule of interest. The nonresonant signal is generally independent of the molecular resonance as it fully results from coupling to virtual levels.



Figure 1.2. Energy level schematic of the particular resonant and nonresonant processes in detected in CARS. Dotted lines indicate virtual levels, continuous lines indicate molecular transitions

The outgoing CARS electric field was well described by Yuratich[69], and then Eckbreth [70], yet here I show the more clear generalized description by Stauffer et al.[62] which defines the outgoing signal as:

$$S_{CARS}(\omega_S, \tau_{12}, \tau_{23}) = |P_{NR}^{(3)}(\omega_S, \tau_{12}, \tau_{23}) + P_{CARS}^{(3)}(\omega_S, \tau_{12}, \tau_{23})|^2$$
(1.1)

Where the resonant and nonresonant third order polarizations are clearly separated, and are dependent upon the intrapulse delays $\tau_{12} = t_2 - t_1$ and $\tau_{23} = t_3 - t_2$. The CARS output is generally dependent upon the detection frequency ω_S . While not detailed in this expression, the nonresonant process is from tremporally overlapped electric fields and is (almost always) slowly varying over a large frequency range, and directly affected by the density of the the gas. The nonresonant part of the third order polarization is molecule dependent and described in the time-domain by:

$$P_{CARS}^{(3)}(t,\tau_{12},\tau_{23}) = \left(\frac{i}{\hbar} \int_{0}^{\infty} dt_{3} \int_{0}^{\infty} dt_{2} \int_{0}^{\infty} dt_{1} R_{4}(t_{3},t_{2},t_{1}) \times E_{3}(t-t_{3}) E_{2}^{*}(t+\tau_{23}-t_{3}-t_{2}) \times E_{1}(t+\tau_{23}+\tau_{12}-t_{3}-t_{2}-t_{1}) \times \exp(i(\omega_{1}-\omega_{2}+\omega_{3})t_{3}) \exp(i(\omega_{1}-\omega_{2})t_{2}) \exp(i\omega_{1}t_{1})$$
(1.2)

This can be described as a convolution of the complex time domain electric fields $E_1(t)$, $E_2(t)$, and $E_3(t)$ in time, with care taken for the appropriate time-delays τ of the incoming pulses and the respective carrier frequencies $\omega_1, \omega_2, \omega_3$. Not detailed is the dependence on phase matching and polarization, which determines the efficiency of the CARS production process, and will be described in a later section.

Initial measurements of CARS were performed using all narrow linewidth laser pulses, which resonated with a specific ro-vibrational molecular level. The output from this could thus be filtered and measured by a photodetector such as amplified photodiode, or photomultiplier tube (PMT). The intensity measured would correspond to the ratio of molecules in the particular state. To obtain the relative population density across many states, the stokes beam ω_2 would be scanned in frequency across different ro-vibrational resonances, as well as through frequencies with very little resonance, in order to quantify the nonresonant contributions. The obtained intensities versus stokes frequency could then be converted to the Raman Shift $\omega_2 - \omega_1$, and used to measure concentration or temperature. A sample schematic from scanning is shown in figure 1.3 below. The advantage of this method is that the collection can be performed with a very sensitive device, and the spectral resolution depends upon the linewidth of the stokes beam. The disadvantage is that scanning the frequency over a sufficient range and with enough resolution often results in a very long measurement time, limiting the application to stable, non-varying combustion environments.

More recently, CARS has been widely applied with the use of a broadband stokes beam. The broadband stokes simultaneously excites all the frequencies of interest. Now the detection has to be performed with a camera and spectrometer to separate the excited resonances created. While the intensity required is much higher now that the pump/stokes preparation



Figure 1.3. (a)Pictorial representation of input and output beams for CARS in a combustion experiment (b) Sample energy diagram with narrowband scanning stokes beam; (c) Sample experimental spectrum from N_2 in a flame at 2225 K, showing Boltzmann distribution over the main vibrational bands

is over a broad frequency range, the advantage of performing single shot measurements enables diagnostics in dynamic and turbulent environments, with the measurement time-scale determined by the laser pulse, and generally on the order of <10 ns. As almost no environment shows significant movement in the 100 μm probe volume over such a time scale, this makes CARS one of the techniques with the best time resolution.

CARS for species concentrations

Concentration could be measured simply by the relative intensity at fewer specific frequencies or in reference to the intensity of the nonresonant background or other molecules. For most molecular gas phase molecules, the CARS signal is expected to be proportional to the squared of the number density of the gas. This means that absolute number density may be determined. As the molecular distribution at higher temperatures is shifted to higher ro-vibrational levels, care must be taken to measure all of the integrated CARS signal; or at least the first ~ 3 vibrational bands. If the temperature is known, then it may be possible, for example to only measure a few points in the $\nu = 0$ vibrational band-head, and so obtain concentration, and molar fraction with the aid of the modeled temperature dependent change in signal.

CARS for temperature measurements

Temperature, instead, is directly obtained by comparing the spectra to a model of the molecule under the assumption of an equilibrium Boltzmann distribution. The Boltzmann distribution is the description of the ensemble molecular distribution throughout all possible states of a molecule at a given temperature. In other words, for a specific temperature, we would expect to find a certain ratio of molecules in the ground vibrational state, compared to the fraction of molecules which happen to be in an excited vibrational state. The fractional distribution can then be further modeled through the electronic, vibrational and rotational states. As this is an ensemble average description it is necessary to probe a sufficient number of molecules to obtain a statistically significant result.



Figure 1.4. Modeled Nitrogen spectra at 500, 1500 and 2000 K showing the increase in the second and third vibrational bands, indicative of more molecules residing in the excited vibrational states

Sample modeled spectra at different temperatures are shown in figure 1.4, where the population increase in the second vibrational band should be quite obvious. At 500 K almost all molecules are in the ground state, while at 1500, and then 2,000 K, a significant population is found in the 2nd excited level, as well as in the third vibrational level (for 2000 K in particular).

1.3 Research objectives

The objective of this thesis is to underline the contributions made to advancing CARS. These contributions can be listed as :

1) Advancement of CARS to other molecules through the demonstration and Characterization of a minor species detection CARS technique for formaldehyde measurements in combustion; and demonstration of increase in stability of the established WIDECARS technique;

2) Increase in the CARS repetition rate to 100 kHz in relevant environments. Highlighted here is the importance of the relevant environment: making a CARS system that didn't just

work on a bench top setting is not trivial, and required addition of uncertainty compensation techniques such as the single shot nonresonant background monitoring;

3) Advance and improvement in the CARS fitting models: this starts from the need of the ps-CARS experiments for a physically accurate model, and is extended as being a model that is effective both for long limit (nanosecond) pulses, as well as impulsive (fs) CARS.

4) Apply the 100 kHz measurement to useful high speed environments to increase the understanding of extremely dynamic events

1.4 Dissertation Summary

This introductory chapter presented a brief overview of the motivation behind the thesis, the applications of CARS in combustion and some additional background on relevant CARS theory and how the measurement enables concentration and temperature measurements. Section 1 of the thesis goes more in depth on nanosecond CARS applied in combustion to enable better modeling of the reactions, showing the addition of ERE-CARS for quantifying minor species concentrations of CH_2O in chapter 2, and the application of the WIDECARS measurement for detection of multiple species with a more stable system in chapter 3. These two chapters are from published papers: the first one was a result of my research at Purdue during the first two years, in the second one (WIDE-CARS), authored by Nicholas Rock, the measurements were performed at Wright Patterson Air Force Base, to show the developed capability of a stable laser system for ultra-broadband multi-species CARS measurements.

The second part of the thesis focuses on the system built and used for 100 kHz Nitrogen vibrational burst-mode ps-CARS. The first chapter provides some general background, followed by the picosecond CARS model and validation in chapter 5. Chapter 6 describes the design and demonstration of the actual 100 kHz picosecond CARS burst-mode system. Chapters 7 and 8 refer to the application of the system in the difficult environments of a fireball, a plasma non-equilibrium environment, and of a high enthalpy shock-tube respectively. Finally the last chapter summarizes the work performed and shifts our focus to the next steps that can be made to enhance and further the usefulness of CARS measurements in today's main applications in hypersonics and high enthalpy environments.

1.5 Author Contributions

Multiple sections of the thesis are from published work, which would not have been possible without the collaboration and contribution of the authors. For this reason I would like to acknowledge here the contributions of each collaborator for the relevant chapters.

Chapter 2 is based upon a paper published in Applied Optics [16]. For the work related to this publication T.R. Meyer and S. Roy obtained funding for the project, and T.R. Meyer provided guidance and direction throughout as my advisor; H.U. Stauffer performed the initial calculations on the energy levels of CH_2O to tune the lasers to, as well as taking the FREE-CARS data mentioned in the comparisons. I set up the CH_2O system, the laser system, performed the experiments, analyzed the data for the calibration and the flame experiments. K.A. Rahman was key in teaching me how to align the dye lasers, as well as in many discussions about the results, thanks to his knowledge from other experiments at elevated pressure. Finally, M.N. Slipchenko provided guidance throughout on the laser setup, how to best acquire the data, and which experiments to perform moving forward to better understand the CH_2O measurement technique.

Chapter 3 is based upon a paper published in Applied Optics [17] The experiments for this were performed at Wright Patterson Air Force Base. P.Wrezinski was the government side sponsor, S.P. Kearney and J. Estevadeordal performed initial developments of the broadband dye laser mixture in a previous summer, S.W. Grib determined the flame and conditions to measure thanks to his expertise in combustion. N. Jiang and P.S.Hsu both worked on obtaining the funded project and making sure it moved forward, as well as having useful suggestions in the experiments, and results interpretation. N. Rahman did further dye optimization, while I optimized the broadband dye lasers, aligned and measured CARS, and provided insight into why and how to get the ultrabroadband output. After the experiments N.Rahman also performed some of the initial data fitting, which he then passed on to N. Rock, who thoroughly analyzed the results and wrote much of the manuscript.

Chapter 5 covers the modeling development, and does not include any published results, but may be partially used for a future publication. Here, while all figures and modeling were performed by myself, I would like to underline the significant influence of many discussions had with H.U. Stauffer and S. P. Kearney on the validity of my modeling approach, and the key contribution by S.P. Kearney who found the correct, strict mathematical derivation which provides self-consistency to the modeling approach taken.

Chapter 6 is based on a paper published in Optics Letters [71]. The development and experiments for this were performed at, and funded by a project through spectral Energies, owned by S. Roy; while himself and T.R. Meyer both provided general objectives guidance. M.N. Slipchenko (my co-advisor) had suggestions on the burst-mode coupling and optimization. While I designed and tested the OPG/OPA system iterations, added the nonresonant background referencing idea, performed the experiments and data analysis; N.Jiang and P.S.Hsu had the initial idea of doing 100 kHz CARS, wrote the proposal from which the project was funded. N.Jiang was present for the H_2/N_2 jet flame experiments, and P.S. Hsu for the DLR flame experiments, as well as both providing insights during the OPG/OPA development.

Chapter 7 is based upon the same system as the one shown in chapter 6, with the application to a fireball and nonequilibrium environment published in a Scitech 2022 conference paper [20] and were also performed at Spectral Energies; so the contribution of S.Roy, T.R. Meyer, P.S.Hsu, and N. Jiang is analogous to that in Chapter 6. For the fireball application, S. Son provided the materials to use, and guidance on which would be the best fireballs to test on, thanks to his energetic materials expertise. A.D.Brown brought the fireball setup, and provided the pyrometry technique. All experiments were performed by myself and A. D. Brown, then I analyzed the CARS and visible imaging, and he analyzed the pyrometry measurements.

Finally, Chapter 8 is based upon the application of the 100 kHz CARS system at the Sandia National Laboratories high enthalpy shock tube facility, also presented at Scitech 2022.[68] M.N.Slipchenko and J. Leicht performed the picosecond burst-mode laser installation at Sandia, I installed the 100 kHz CARS system and performed the initial CARS shock tube measurements, and data analysis; S.P.Kearney managed the project, and performed and took over successive experiments and analysis after I left. C.R. Downing ensured smooth operation of the shock tube components and pressure system. The shock-tube runs and conditions decisions were lead by J. Wagner, and put into action by K.P. Lynch. K.A. Daniel ran the imaging camera, and assisted K.P. Lynch in the operation of the shock-tube, and condition prediction.

Part I

ADVANCEMENT OF CARS FOR SPECIES DETECTION IN COMBUSTION

2. CONCENTRATION AND PRESSURE SCALING OF CH₂O ELECTRONIC-RESONANCE-ENHANCED COHERENT ANTI-STOKES RAMAN SCATTERING SIGNALS

Modified from a paper published in Applied Optics 60, 4 1051-1057 (2021) Daniel K. Lauriola, K. Arafat Rahman, Hans U. Stauffer, Mikhail N. Slipchenko, Terrence R. Meyer, and Sukesh Roy

Nanosecond electronic-resonance-enhanced coherent anti-Stokes Raman scattering (ERE-(CARS) is evaluated for the measurement of formaldehyde (CH_2O) concentrations in reacting and non-reacting conditions. The three-color scheme utilizes a 532 nm pump beam and a scanned Stokes beam near 624 nm for Raman excitation of the C–H symmetric stretch (ν_1) vibrational mode; a 342 nm resonant probe is tuned to produce outgoing CARS signal via the $1_0^1 4_0^3$ vibronic transition between the ground $(\tilde{X}^1 A_1)$ and first excited $(\tilde{A}^1 A_2)$ electronic states. This allows detection of $\rm CH_2O$ at concentrations as low as $9\cdot 10^{14}$ molecules/cm³ (55 parts per million) in a calibration cell with CH_2O and N_2 at 1 bar and 450 K with 3% uncertainty. The measurements show a quadratic dependence of signal with CH₂O number density. Pressure scaling experiments up to 11 bar in the calibration cell show an increase in signal up to 8 bar. We study pressure dependence up to 11 bar, and further apply the technique to characterize the CH₂O concentration in an atmospheric premixed dimethyl ether/air McKenna Burner flame, with a maximum concentration uncertainty of 11%. This approach demonstrates the feasibility for spatially resolved measurements of minor species such as CH₂O in reactive environments and shows promise for application in high-pressure combustors.

2.1 Introduction

The accurate measurement of minor-species concentrations, such as that of formaldehyde (CH_2O) , is necessary for emissions monitoring and can play a key role in understanding the thermochemistry of various combustion processes [72], [73]. Because formaldehyde is a known carcinogen and pollutant, it is important to measure atmospheric CH_2O with parts per million (ppm) sensitivity [28]. In combustion, formaldehyde is an important intermediate for the oxidation of hydrocarbons. It is used to detect the presence of cool flames [74], visualize flame fronts [75], measure ignition delay [76], and provide modeling insight on numerous intermediate chemical reactions [77]. As such, background free, spatially resolved measurements of ppm levels of formaldehyde in reactive and non-reactive environments are of fundamental and practical interest. Additionally, formaldehyde is one of the simplest asymmetric top molecules, representing a benchmark for more complex molecules.

Various experimental techniques have been applied in the gas phase to either confirm the molecular structure, or provide information to combustion models for the oxidation of CH_2O . Absorption spectroscopy (AS) and four-wave mixing have been employed to investigate the rotational structure of the electronic ground [47], [78] and excited states [48], [79], [80], while Fourier transform infrared spectroscopy (FTIR) has been used to measure CH_2O concentrations in gas samples collected from a dimethyl ether (DME) flame [81]. CH_2O planar laser-induced fluorescence (PLIF) has allowed determination of the two-dimensional distribution of formaldehyde in applications such as turbulent flames [18], [30], [42], [45], [82], [83], high-pressure environments [39], across shock waves [84], and to mark the ignition zone in a scramjet engine. Demonstration of qualitative CH_2O PLIF has been accomplished at repetition rates as high as 100 kHz [85], and the intensity change in the PLIF signal has also been used as a semi-quantitative technique in DME flames [76]. Many of the described techniques for measuring concentration suffer from spatial resolution limitations, line-of-sight averaging (AS [47], [48], FTIR [81]), or sensitivities to the molecular quenching environment (PLIF) [18], [30], [39], [45], [84].

Spatially resolved, quantitative background-free measurements of many combustion species over varying pressures have been made possible by coherent anti-Stokes Raman scattering spectroscopy (CARS). CARS is a non-linear optical technique that targets transitions of vibrational or rotational energy states of a polarizable medium using the frequency difference between two electric fields (pump and Stokes). The Raman resonances that exist near the pump/Stokes difference frequencies are subsequently probed by a third electric field (probe). The method is widely used in combustion because it allows for excellent spatial resolution and can be background free with the appropriate experimental arrangement. Variations of CARS have been widely used for temperature and major species concentration measurements [12].

Recently, femtosecond CARS [86] has been used to study the rotational structure of the S_0 $(\tilde{X}^1A_1))$ ground electronic state at 80 mbar and to improve accuracy of Raman spectral modeling of CH_2O , where Coriolis interactions between different levels affect the strength and position of lines in the ground electronic state ν_1 (symmetric C–H stretch) vibrational level near 2782 $\rm cm^{-1}$. As CARS signals scale quadratically with the absolute number density of the probed molecule, measurements can be limited to chemical species with relatively high concentrations. For low-concentration measurements in a combustion environment, electronic-resonance-enhanced (ERE) CARS has been shown to be a promising technique [8]. In this variation of CARS, one or more of the laser wavelengths is tuned to access an electronic resonance of the molecule. Coupling the pump or probe beams to an electronic level, instead of to a virtual state, can increase the signal level a thousand-fold, enabling ppm-level detection. ERE-CARS has already been demonstrated as a spatially resolved technique in a flame for the detection of NO [54], [87], C₂ [87], and OH. Attal-Trétout et. al. [49] measured the OH concentration in a high-pressure environment, and Wrzesinski et. al. [51] used femtosecond fully resonant electronically enhanced CARS (FREE-CARS) of OH for simultaneous flame temperature and concentration measurements.// In this work, we demonstrate ERE-CARS of CH_2O , allowing quantitative concentration measurements at low ppm mole fractions in both reacting and non-reacting environments. Access to the Raman-active fundamental transition of the ν_1 band of the ground S_0 electronic level of CH₂O is achieved by tuning the Stokes beam wavelength (~ 624 nm) relative to a fixed pump wavelength (532nm), whereas electronic enhancement results from a UV probe wavelength (~ 342 nm) that couples these states to the (1,0,0,3,0,0) vibronic band of the first singlet S1 (\tilde{A}^1A_2) excited
state (Fig.2.1a), producing outgoing CARS signal (~312 nm) via $1_0^1 4_0^3$ vibronic transitions. Using this optical setup, we have characterized the pressure and concentration scaling of the CH₂O ERE-CARS signals in a non-reacting mixture with N₂. Application of this technique toward concentration measurements of CH₂O was subsequently demonstrated in a premixed dimethyl ether (DME)/air flame stabilized over a McKenna burner at atmospheric pressure.

2.2 Experimental Apparatus

As shown in Fig.2.1b, the experimental setup employed an injection-seeded Nd:YAG laser (Spectra Physics, GCR-3) providing 700 mJ/pulse second harmonic (532 nm) output at 10 Hz; the spectral linewidth (full width at half maximum, FWHM) of this output was measured (HighFinesse WS7 wave meter) to be 0.02 cm^{-1} . The 532 nm pump beam in the ERE-CARS scheme was produced by splitting off 10% of this output energy; the remaining was subsequently split with a 50/50 beam splitter to pump two narrowband single-grating dye lasers (Continuum, ND6000). In the first dye laser, a mixture of DCM dye (Exciton) and ethanol was used to produce a 50 mJ/pulse Stokes beam, (15% conversion efficiency), tunable from 15,966 to 16,052 cm⁻¹ (~623-626.3 nm), with a measured linewidth (FWHM) of 0.1 cm⁻¹ and < 10% pulse-to-pulse energy variation.

In the second dye laser, LD688 dye (Exciton) and methanol were mixed to generate output that was subsequently frequency-doubled in a Type-I α -barium borate (α -BBO) crystal to produce the probe beam, tunable from 29,200 to 29,450 cm⁻¹ (\sim 339.6-342.5 nm), with a measured linewidth of 0.2 cm⁻¹ (FWHM), and UV energy of 17 mJ/pulse (5% 532 nm to 342 nm conversion). The wavelengths and energies at each step were recorded during the experiment for use in post-processing of the measured ERE-CARS spectra.

Per-pulse energy adjustment of the pump and probe beams was performed using half-wave plate (HWP) and polarizer combinations, whereas neutral density filters were used for attenuation of the Stokes beam. For the experiments in the pressure vessel, the beams were all vertically polarized. However, for experiments in the McKenna burner, polarization-based non-resonant background suppression was necessary to remove the contribution from the hydrocarbons present in the dymethyl ether flame. This was accomplished by setting the pump and Stokes polarizations at 60° with respect to vertical, and an α -BBO polarizing beam splitter on the detection side was set to 30°, perpendicular to the non-resonant background signal. This polarization configuration produced a 10⁴ attenuation of the non-resonant background while incurring only a tenfold loss in the resonant signal [8], [10].

The beams were directed into the probe volume in a folded BOXCARS arrangement [7]. The incoming beams were focused, and the outgoing ERE-CARS signal subsequently recollimated using 150 mm focal length plano-convex lenses (UV-grade fused silica). On the output, a physical mask was used to block the pump and Stokes beams, and the probe beam was directed into an energy monitor. The CARS signal beam was reflected by a 45° narrowband high reflector at 312 nm into three 310 nm band-pass filters (Edmund Optics, 34976, 10 nm FWHM) and a UV short-pass filter (Thorlabs, FGUV11M) to eliminate any stray scattering of the input beams before being measured by a UV sensitive photomultiplier tube (Hamamatsu R9110). The photomultiplier tube was connected to an oscilloscope (Rigol, 1000Z), controlled by a LabVIEW VI, used to save single-shot or averaged traces to the computer for post-processing analysis.

A typical scan, depending on the range and resolution, lasted 10-25 minutes with 64 laser shots being averaged for each step of the stokes or probe wavelength scan.



Figure 2.1. (a) Formaldehyde energy level diagram. The fundamental ν_1 vibrational band of ground state (S0) CH₂O was probed; probe resonance with the excited electronic state (S1) was used for signal enhancement. (b) Three beam ERE-CARS setup. BS - beam splitter; Pol - polarizer; ND - Neutral density filter; BBO - beta barium borate crystal; TFP - thin film polarizer; DM - dichroic mirror; $\lambda/2$ - half wave plate; PBS - α -BBO polarizing beam splitter. At the probe volume, depending on the experiment, either a non-reacting pressure vessel or a premixed flat flame stabilized McKenna burner were used.

An optically accessible mixing chamber rated up to 30 bar with four 0.25"-thick UV fused silica windows was used for conducting high-pressure experiments in an N2 and CH_2O mixture. The mole fractions of N₂ and CH_2O were set by the following procedure, similar to that used by Walser et al. [88], [89]: a 37% CH_2O aqueous solution (Fischer Scientific) was first placed in a windowless stainless-steel evaporation chamber shown in 2.2(a); the

evaporation chamber was heated to 475 K with heating tape, and the pressure vessel was evacuated and heated to 450 K; after 20 minutes, the valve between the chambers was slowly opened, and the gas passed through a colder section (360 K) to condense out some of the water before entering the windowed vessel; after a few minutes, the test chamber was again isolated from the evaporation chamber with a manual valve; heated N₂ was then slowly added from a separate port to attain the desired pressure. As previously reported in refs. [48] and [88], every time the vessel was cooled down to room temperature, a white film of polymerized CH₂O formed on the inner walls, requiring cleaning; and in the first experiments coating of the windows was a significant issue which lead to beam scattering and absorption. To avoid polymerization, the pressure vessel was completely wrapped in heat tape, and hot air jets were directed at the windows. This system was designed to mix CH₂O in an N₂ environment with a mole fraction as low as 55 ppm at 1 bar. The uncertainty in the mixture fraction of CH_2O was approximately 5% at pressures from 0.5 to 11 bar, and the temperature was set at 450 K for the experiments in the pressure vessel. For experiments with the DME/air flame, a flat-flame porous plug McKenna burner, analogous to the one described in ref. [81], replaced the pressure vessel. Saturation of the CARS signal as a function of the energy of each of the CARS beams was measured, and it was found that the energy in the pump and Stokes beams must remain under 10 mJ/pulse, whereas the probe energy must be under 2 mJ/pulse, to avoid saturation. During the experiments in the pressure vessel, energies for each beam were kept at or below 3 mJ/pulse to also avoid damage to the windows and corresponding degradation of the input beams.



Figure 2.2. (Camera picture of the formaldehyde preparation setup showing a)Vacuum pump, evaporation chamber (bottom left), experimental pressure vessel (top) and CH_2O capture system consisting of two cold containers of neutralizer solution; b) Pressure vessel wrapped with heat tape to maintain the required temperature.

2.3 Results and discussion

2.3.1 Mixing chamber calibration

Characterization of the spectral response of the ERE-CARS signal was performed by scanning either the Stokes or probe frequencies during measurements of CH₂O in N₂ (mole fraction = 700 ppm) at 450 K and 1 bar in the pressure vessel described in the experimental setup. Initially, the Stokes-beam frequency was fixed to access the fundamental $\nu 1$ bandhead at a Raman shift of 2782.5 cm^{-1} [90], while the probe frequency was scanned from 29,230 to 29,300 cm^{-1} (step size of 0.2 cm^{-1}). An average of two probe-frequency scans is shown in Fig.2.3 a, performed with a pump and Stokes energy of 2 and 3 mJ/pulse respectively, and a wavelength-dependent probe energy between 0.3 and 1 mJ/pulse. The results have been corrected for probe-pulse intensity variance with wavelength. The scan in Fig.2.3a, therefore, shows the wavelength dependence associated with electronic resonance enhancement of CARS signal via the $1_1^1 4_0^3$ vibronic transition. Prior ERE-CARS experiments with NO have demonstrated broad resonance enhancement, with peaks spaced about 40 cm^{-1} [54], while for CH_2O we observed two close separate peaks in the electronic resonance enhancement. Although the $1_1^1 4_0^3$ transition band of CH₂O has not been explicitly studied previously, these excitation features are consistent with comparable features observed in high-resolution scans of the $1_0^1 4_0^3$ absorption band, where two close distinct peaks were present at the transitions corresponding to the outgoing CARS signal of the probe scan [48]. While direct absorption might not take into account the resonant features of the ERE-CARS interaction, higher resolution measurements of CH₂O performed using FREE-CARS in our laboratory (not shown here) also exhibit two well-resolved, strongly resonant rovibronic peaks $\sim 20~cm^{-1}$ apart. While the probe scan range was limited here by the probe dye laser wavelength range, excitation scans by Bouwens et al. [91] as well as CH_2O FREE-CARS excitation-wavelength scans suggest that significantly stronger resonance enhancement might be obtained by using a probe redshifted by $\sim 200 \ cm^{-1}$. Exploration of different electronic enhancements could be an interesting application for further studies if higher sensitivity is of interest.



Figure 2.3. (a) Electronic level splitting and its effect on the rotational levels of fundamental transition of the ν_1 vibrational mode. (a) Average of 2 wavelength scans of the probe beam at atmospheric pressure with 700 ppm of CH₂O in N₂ at 450 K. The Stokes beam was tuned to a Raman shift of 2782.5 cm^{-1} relative to the pump beam, and the probe beam was scanned in steps of 0.2 cm^{-1} . Each point was averaged over 64 laser shots. (b) Signal from wavelength scans of the Stokes beam for 2 different denoted probe frequencies tuned within the electronic resonance band. Scans were performed with a step size of 0.05 cm^{-1} and 64 shot average for each step. Inset in (b) shows a detail of the scans divided by the resonance enhancement measured in (a).

Figure 2.3 b shows scans of the Stokes beam with a probe wavelength fixed at 29,260 cm^{-1} and 29,272 cm^{-1} respectively (see Fig.2.3 a), while the Stokes beam was scanned with a 0.05 cm^{-1} step from a Raman shift of 2770 cm^{-1} to 2790 cm^{-1} . The first scan, with probe at 29,260 cm^{-1} , was performed three times at the same CH₂O/N₂ conditions to measure a 3% uncertainty in the scan repeatability. The resulting locations of the K_a levels were in agreement with the Coriolis-shift perturbation model and experimental fs-CARS measurements presented by Walser et al. [86], as well as the Raman spectra by Magnotti et al. [29]. The higher resolution scans of this experiment showed the wrapping of the bandhead predicted by Walser et al., the overlap of the $K_a=1$ and $K_a=2$ levels, as well as line strength differences in scans performed at the two probe wavelengths. The difference in the two scans can be understood based on the energy levels diagram shown in Fig. 1b. The ro-vibrational band reached in the S1 excited electronic level depends on all three frequencies: $\omega_4 = \omega_1 \omega_2 + \omega_3$. During the Stokes scans, ω_1 and ω_3 are held constant, and ω_2 is scanned through different $(\omega_1 - \omega_2)$ Raman shifts, causing ω_4 to change with ω_2 . As this Raman shift is varied to access different intermediate transitions, the probe accesses different final transitions within the S1 excited electronic level, and the outgoing signal intensity will depend on both the $(\omega_1 - \omega_2)$ intermediate levels, as well as the transition probabilities into and out of the levels accessed by the probe, further complicating modeling of the spectra.

Direct comparison between the two scans was achieved via normalization of the spectra by the electronic resonance enhancement measured in Fig.2.3 a: by knowing the initial probe and stokes frequencies, w4 was matched to map the probe scan onto the Stokes scans. The Stokes scan was then divided by the matched probe scan to normalize out the resonance enhancement. This correction was applied to each scan in Fig.2.3 b, (see inset Fig.2.3 b). The electronic enhancement normalization worked for the $K_a=3-5$ levels, but did not completely match the band head ($K_a=1,2$), where the resonance probability appears to vary too significantly, as the resonance enhancement with the probe fixed at 29,272 cm⁻¹ falls abruptly above 2782.5 cm⁻¹. Differences in the two scans may also result from different transition probabilities into S_1 for different Raman shifts. While outside the scope of this paper, multiple probe scans at different Raman shifts would be necessary to fully study the effects of the transition probabilities on the two scans. The goal of the current experiment was to perform measurements in a region of constant electronic resonance, so the probe was set to the broadest of the two electronic transitions (29,260 cm^{-1}), providing sufficient enhancement for the range of Raman shifts from 2775 to 2784 cm^{-1} and with a rapid drop-off outside this range. This choice of the probe wavelength enabled measurements of the $K_a = 1-5$ transitions of the ν_1 vibrational band of the S_0 electronic level with little change in resonance, while higher K_a transitions remained outside of the maximum resonance enhancement and below the detection limit at atmospheric pressure.



Figure 2.4. (a) Scans performed at atmospheric pressure with increasing concentrations of CH₂O in N₂ to calibrate the technique for different concentrations and estimate a detectability limit. Scans were performed with a 0.2 cm^{-1} step size and 64-point averaging. (b) Concentration scaling at different pressures. The data points were obtained by integrating the intensity of the spectral scan from 2775 cm^{-1} to 2785 cm^{-1} . Solid lines represent the linear fits.

The scaling of CH_2O ERE-CARS signal with concentration was performed in a mixture of CH_2O and N_2 at three different pressures. The probe laser was set to 29,260 cm^{-1} , and the Stokes dye laser scanned across a Raman Shift of 2760 to 2790 $cm^{-1},$ with a 0.2 cm^{-1} step size and 64-point averaging. The spectra shown in Fig. 2.4a were integrated between 2775 and 2785 cm^{-1} for each concentration. The square root of the result was plotted in Fig. 2.4b, with a linear fit for each condition. At atmospheric pressure, a maximum signal-tonoise ratio (SNR) of 2,000 was achieved for a concentration of 1.14×10^{16} molecules/cm³ of CH_2O (mole fraction of 700 \pm 20 ppm, calculated from amount of CH_2O and N_2 pressure). An SNR of 10 was achieved for the lowest measured concentration of $9 \cdot 10^{14}$ molecules/cm3 (mole fraction of 55 ± 20 ppm). The detection limit was estimated at $2 \cdot 10^{14}$ molecules/cm³ for an SNR of 1 (molar fraction of 12 ppm), although this concentration of CH₂O was too low to be accurately dispensed in the current system. As seen in Fig. 3a, the non-resonant signal from 100% $\rm N_2$ remained constant across the spectrum, much lower than the resonant signal. The square root of the CARS signal intensity was found to be linear with number density, as was also observed previously in ERE-CARS experiments with other molecules [87] and can be inferred from theory, which predicts the intensity of CARS signal is proportional to the square of the number density [6]. The experiments for 2.4b were performed at constant pressures of 1, 3 and 5 bar, respectively, exhibiting a similar number density dependence. Above atmospheric pressure, the slope of the concentration scaling fit decreased, indicating that the effects of pressure may already have an influence from 3 bar. To test the influence of pressure on the concentration scaling, further experiments were performed in which the mole fraction of CH₂O was kept constant and the pressure was increased.

Figure 2.5a shows a sample of scans at pressures ranging from 1 to 11 bar. Each data point in Fig.2.5b was calculated by integrating the spectra between 2775 and 2785 cm^{-1} , after non-resonant background subtraction, and shows two independent measurements. Fig. 2.5b shows that as pressure is increased, the signal does not follow the squared number density scaling. The signal increases slowly with pressure and flattens out above 8 bar. The deviation from the theoretically predicted squared number density dependence at high pressures was previously observed in ERE-CARS measurements of other species [12], [49]. Absorption experiments at high pressure showed up to 10% of the input 29, $260cm^{-1}$ probe beam energy was absorbed at 8 bar, but this is not enough to account for the flattening of the signal [92]. The deviation is likely caused by two factors: collisional line broadening in both the electronic levels, and re-absorption of the outgoing CARS beam. The indication of the line broadening associated with the final electronic transition is most obvious in the scan at 11 bar (Fig.2.4 a), in which higher excited $K_a = 7$ and 9 levels appear, suggesting that the electronic resonance has broadened sufficiently to bring transitions from these higher K_a states into resonance, and plays a nontrivial role in the flattening of the signal.



Figure 2.5. (a) (a) Stokes scans at a constant mole fraction of 700 ppm in N_2 and increasing pressures, which results in a linear number density increase with pressure. Scan step size of $0.2 \ cm^{-1}$ and 64 point averaging were used. The scan at 11 bar was performed with a 0.05 cm^{-1} step size. Pump, stokes, probe energies were set to 2, 3, and 0.5 mJ respectively (b) Square root of the integrated intensity under the curve between 2775 and 2785 cm^{-1} of the highest peak (~2782 cm^{-1}) after non-resonant background subtraction. Error bars in x of 0.1 bar and 3% in y. Test 1 and test 2 indicate scans performed on different days.

As the outgoing CARS signal wavelength matches the $1_0^1 4_0^3$ vibronic transition of CH₂O, re-absorption of the CARS signal through this same transition could also play a significant role in the signal flattening at higher pressures and number densities. While further study of these effects is beyond the scope of this publication, the pressure scaling experiments show that the ERE-CARS technique can be used at least up to 11 bar, and indicate that it is necessary to perform a constant pressure concentration calibration for the pressure expected during the experiment.

2.3.2 Application to dimethyl ether flame

CH₂O ERE-CARS was tested in the reacting environment of an atmospheric pressure premixed DME/air flat-flame burner. This particular flame was selected because it could be compared to the publication by Kaiser et al. [81] in which a thorough characterization of CH₂O concentration in a DME/air flame was performed using FTIR on gas samples extracted with a physical probe. The 25.4 mm diameter water-cooled McKenna flat-flame burner was mounted on a vertical translation stage, in place of the pressure vessel. Polarizationbased non-resonant-background suppression was applied after experiments showed the nonresonant contribution of unburnt DME to be $\sim 5\%$ of the resonant signal. An image of the flame, the samples of three repeated Stokes scans in the DME flame at $\phi = 1.3$, and a calibration scan from the pressure vessel are shown in Fig. 2.6. The energies used for the flame were 6 mJ/pulse for the pump and Stokes beams and 1.5 mJ/pulse for the probe beam. Three scans were performed for each equivalence ratio, then each data set was integrated from 2775 to 2785 cm^{-1} and calibrated with the integrated signal from the pressure vessel and the temperature dependent number density of the flame. The standard deviation from multiple scans was used to estimate the uncertainty, which reached a maximum of 11% for the richest conditions ($\phi = 1.64$ and $\phi = 2.19$), where the flame also appeared unstable and likely contributed to increased signal fluctuations.



Figure 2.6. (Sample of three Stokes scans with a step size of 0.1 cm^{-1} at $\phi = 1.3$ and 0.75 mm above the burner surface. These scans were used to determine the uncertainty in the flame measurements, and the scan with $4.7 \cdot 10^{16} \ molec \cdot cm^{-3}$ of CH₂O was performed in the pressure vessel for calibration. Inset: Image of the Mckenna burner flame at $\phi = 1.3$ with N_2 co-flow.

The vertical translation stage was moved from 0.25 to 1.75 mm above the burner with a 0.25 mm step, for a rich and a lean flame condition (Fig. 2.7a). The results were plotted with the physical probe sampling data from Kaiser et al. [81], with the stated $\pm 10\%$ precision. Both show an increase of CH₂O concentration in the pre-mix zone, and then a drop in the downstream, where the flame is hot and CH₂O is turned into reaction products. Downstream of the flame front the CH₂O concentration rapidly decays. For the $\phi = 0.67 \pm 0.05$ condition, the visible flame is much broader, and the change in CH₂O concentration is less pronounced in the upstream and in the downstream sides of the flame. Comparison of our results with the data from the physical probe experiments of Kaiser et al. [81] shows that the trends agree well in the pre-flame zone, but after the flame front our concentration measurements show

a slower decay in the CH₂O concentration (see Fig. 2.7a). The most apparent difference between the two experiments is that the ERE-CARS measurement is an in-situ measurement, while in the previous method a sample is first extracted from the flame and then analyzed. It is possible that the probe quenched the flame, or that further reactions from CH₂O into products weren't interrupted quickly enough during the sampling. Small differences in the mass-flows and in the absolute flame position are also probable and may explain the peak offset in the $\phi = 1.49$ condition.



Figure 2.7. (a) Concentration measurements for height scans at rich and lean flame conditions in a pre-mixed DME/air McKenna burner. Concentration was obtained by integrating the signal from 2775 to 2785 cm^{-1} , calibrated with measurements in the pressure vessel. The height above burner indicated the height of the probe volume above the top surface of the burner. The zero was set to where the probe volume hit the top surface of the burner. Y error bars are the standard deviation of multiple measurements, and x error bars represent the 0.05 mm uncertainty from the micrometer. Also shown are measurements by Kaiser et al. [81] in an analogous burner. (b) Concentration measurements of an equivalence ratio scan 0.75 mm above the burner. The x error bars represent ± 0.05 uncertainty in the equivalence ratio, and the y error bars are from the standard deviation of multiple trials.

Overall the general trends are in agreement for the two experiments. Further experiments, shown in Fig. 2.7b, were performed by varying the equivalence ratio at a fixed height of 0.75 mm above the burner. The same experimental conditions of Fig. 2.7a were used, and the equivalence ratio was varied from 0.4 to 2.1. The specific height was selected because it is right before the flame front, where CH₂O oxidation should occur. Fig. 2.7b shows a linear increase in CH₂O concentration in the oxidation layer up to a stochiometric flame, with a peak concentration around $\phi = 1.6$. As a comparison for these results could not be found in literature, this measurement may be used as a guideline for modeling the CH₂O concentration in the oxidation flame.

2.4 Conclusion

In this work, quantitative ERE-CARS measurements of the CH₂O concentration were performed in a high-pressure mixing chamber and in a premixed DME/air flat-flame. Characterization data showed two close transitions in the $1_1^1 4_0^3$ vibronic transition band that could each provide electronic enhancement of the CARS signal mediated by the Raman-active ν_1 vibrational band of the ground electronic state. The measurements showed that the technique is effective at mole fractions lower than 55 parts per million of CH_2O in N_2 at 450 K, with an estimated detectability limit of 12 ppm. The quadratic dependence of the signal on the concentration was in agreement with expected CARS concentration dependence and was used as a calibration for experiments in a flame. The scaling of the signal with pressure also revealed transition line-broadening effects up to 11 bar. The pressure effects were apparent as low as 3 bar, but the signal increased with pressure-dependent number density up to 8 bar, above which it remained constant. Furthermore, application of the technique to a premixed dimethyl ether/air McKenna flat flame burner yielded a similar trend to that shown in previous literature, allowing additional characterization of the CH_2O concentration of this flame at varying heights and equivalence ratios with a precision of 11% or better. This was the first application of ERE-CARS measurements for CH₂O concentration, and the first application of a CARS technique to measure CH_2O concentration in a flame and in a high-pressure environment.

This technique could be used extensively in high-pressure combustion measurements where modeling is still lacking and good knowledge of the reaction processes obtained by the measurement of formaldehyde. Combining the measurement with others, such as WIDECARS to provide temperature, and additional species information, would enable a more complete picture of the reaction rates in high pressure flames.

3. WIDECARS MULTI-PARAMETER MEASUREMENTS IN PREMIXED ETHYLENE–AIR FLAMES USING A WAVELENGTH STABLE ULTRABROADBAND DYE LASER

Modified from a paper published in Applied Optics, vol. 59, No.8, March 10th 2020 Nicholas Rock, Paul S. Hsu, Daniel K. Lauriola, Naveed Rahman, Jordi Estevadeordal, Stephen W. Grib, Naibo Jiang, Sean P. Kearney, and Paul Wrzesinski

This chapter highlights the demonstration of a technique to measure temperature and mutiple species with a stable laser, making WIDECARS more relevant for applied measurements.Rather than basic technique development, the advances highlighted here are in the use of a more stable broadband dye laser, which makes the technique more useful for field measurements. After the experiments, performed by myself and some of the authors, as detailed in the introduction, most of the data analysis was performed by Nicholas Rock.

Width-increased dual-pump enhanced coherent anti-Stokes Raman spectroscopy (WIDE-CARS) measurements were used to determine the temperature and major species mole fractions in laminar, premixed, ethylene-air flames operating at atmospheric pressure. Conventional ultrabroadband dye lasers for WIDECARS, which use Pyrromethene dyes, have historically suffered from day-to-day wavelength shifting. To overcome this problem, a new ultrabroadband dye laser was developed in this study to provide a stable wavelength and power generation. A new dye laser pumping scheme and a mixture of Sulforhodamine 640, Kiton Red 620, and Rhodamine 640, was used to generate the desired FWHM ~15 nm $(410cm^1)$ bandwidth. The WIDECARS measured mole fraction ratios of CO_2 , CO, and H_2 with N_2 agreed well with chemical equilibrium calculations.

3.1 Introduction

Coherent anti-Stokes Raman spectroscopy (CARS) has been widely used for temperature and species concentration measurements in reacting flows with high spatio-temporal resolution [12]. However, narrow Stokes beam bandwidths limit traditional CARS to only measuring a single species, typically N_2 , which is nearly inert and exists everywhere in most combustion experiments. To overcome this challenge, dual-pump CARS [93], triple-pump CARS [94], and dual-pump dual-broadband CARS [52], [95] technologies were developed to make simultaneous measurements of multi-species mole fractions and temperature. For example, dual and triple-pump CARS systems have allowed the mole fractions of CO_2 [96], O_2 [93], H_2 [97], CO [97], C_2H_4 , and CH_4 [98] to be measured in addition to N_2 . These techniques involve using a tunable narrowband dye laser to shift the wavelength of the pump beam away from the wavelength of the probe beam. An appropriately selected wavelength for the narrowband dye laser allows both beams to interchangeably act in the probe and pump roles for two species, and the corresponding CARS signals from these species will be generated at similar wavelengths. Width-increased dual-pump enhanced coherent anti-Stokes Raman spectroscopy (WIDECARS) introduced the capability to simultaneously measure the temperature and mole fractions of most major species in hydrocarbon combustion reactions. WIDECARS [99] is conceptually similar to dual and triple-pump CARS, but it increases the number of detectable species by using an ultrabroadband dye laser as the Stokes beam. The Stokes beam used in the original WIDECARS system [99] had a FWHM of ~17.4 nm (480 cm^{-1}), centered near 602 nm. It enabled simultaneous measurements of the gas temperature from N_2 , and concentrations of CO_2 , CO, O_2 , H_2 , C_2H_4 , and N_2 . A mixture of Pyrromethene 597 and Pyrromethene 650 dyes was used in the oscillator of this ultrabroadband dye laser, while a mixture of Rhodamine 610 and Rhodamine 640 was used in the amplifier [99]. The ultrabroadband dye laser was later modified in Ref. [100] to achieve a FWHM of ~23 nm (640 cm^{-1}), which allowed additional H_2 and C_2H_4 bands to be probed. This modified design involved mixing Pyrromethene 597 and Pyrromethene 650 in both the oscillator and amplifier dye cells [100]. It was originally characterized on a premixed ethylene–air McKenna. burner flame [100] and has since been used to study scramjet applications [100], [101]. Traditional ultrabroadband dye lasers that have been previously used for WIDECARS have often produced unstable spectral profiles and energy outputs. This is because these lasers used Pyrromethene dyes, which are known to decay more rapidly than Rhodamine dyes [99], [102]. For example, non- resonant argon spectra measured in Ref. [100], which solely utilized Pyrromethene dyes to produce the Stokes beam, shifted $\sim 1.1 \text{ nm}$ [101] between the beginning and the end of an experimental test day. Furthermore, these non-resonant argon spectra were observed to vary\$10% shot-to-shot at certain wavelengths [101], although changes in both the phase-matching efficiency and mode noise in the broadband dye laser contribute to these fluctuations. The time history of the measured nonresonant argon spectra provides a good indication of the accuracy for a WIDECARS system because the spectral profile of the Stokes beam, the phase-matching efficiency, and errors in the detection system manifest themselves in these spectra. However, they are also involved in a key data pre-processing step, as each measured CARS spectrum is normalized by a mean non-resonant argon spectrum to remove the characteristics of the Stokes beam. Therefore, changes in the Stokes beam over the time of the experiment can introduce errors caused by instantaneous fluctuations around the average spectral profile and systematic errors, caused by shifts in the peak wavelength of the Stokes beam, when the CARS spectra are analyzed. Since there is not an effective method to date for concurrently measuring a non-resonant argon spectrum and the flame, it is critical that the Stokes beam remains stable throughout the duration of an experiment. In this study, a wavelength and power stable ultrabroadband dye laser for WIDECARS was developed. The measurement accuracy and precision of this improved WIDECARS system were validated using a McKenna burner. The temperature and species distributions for the McKenna burner were characterized at various equivalence ratios and spatial locations for further validation.

3.2 Experimental setup

A schematic of the WIDECARS experimental setup is shown in figure 3.1. A 10 Hz Nd:YAG laser (Spectra-Physics PRO-290-10H) produces a 532 nm laser beam with a pulse duration of 10 ns and an energy of 1.2 J/pulse. Approximately 400 mJ/pulse and 700

mJ/pulse are used to pump narrowband (centered at 556.5 nm) and broadband (centered at 605 nm) dye lasers, respectively. The remaining 100 mJ/pulse of the 532 nm beam acts as the second interchangeable pump/probe beam. These three beams were spatially overlapped in the probe volume using a folded-crossed-beam phase-matched CARS (BOXCARS) beam geometry. A f = +300 mm lens was used to focus the three laser beams. The three original beams and the generated CARS beam (~495 nm) were re-collimated using a 300 mm focal length lens. The pulse energies were 25, 35, and 34 mJ/pulse for the 532 nm, 556.5 nm, and broadband Stokes beams, respectively. The CARS beam was routed to a 3/4 m spectrometer with an 1800 grooves/mm grating. The dispersed CARS signal was recorded using a non-intensified back-illuminated CCD camera. The spectral dispersion of the detection system was measured to be ~0.40 cm^{-1} /pixel.



Figure 3.1. Schematic of the WIDECARS setup. PBS, polarizing beam splitter; NBDL, narrowband dye laser; BBDL, broadband dye laser.

Most of the spectra were recorded by averaging signal from five laser shots on the camera (fuel-lean and nearly $\phi = 1$ cases). To avoid signal contamination by resonant Raman features from gas-phase C_2 [103] produced by ablation of native soot particles by the intense CARS beams, the energy of the 532 nm laser beam was intentionally reduced to 15 mJ/pulse for the very fuel-rich cases (e.g., $\phi = 2.06$). Thus, a lower CARS signal resulted for these cases

and greater signal averaging (~100 laser shots) was employed. WIDECARS measurements were sampled at the geometrical center of a premixed, ethylene–air McKenna burner. The steel surface of the McKenna burner was water-cooled, and an annulus of N_2 flowed around the 60 mm diameter sintered bronze burner element to prevent a C_2H_4/air diffusion flame from forming at the burner edge. Room-temperature air served as the oxidizer for the flame and had a fixed flow rate of 18.8 standard liters per minute (SLPM). The flow rate of ethylene was adjusted such that the tested equivalence ratios ranged from $\phi = 0.50$ to $\phi = 2.06$. The burner was fastened to a translation stage to allow measurements to be made at different heights above the burner surface (HAB). Measurements were taken at HAB = 1–4 cm for each of the studied equivalence ratios. Unlike many other studies that have been conducted using a McKenna burner [100], [103], a stabilization plate was not placed above the burner. This caused the downstream portion of the flame to flicker during the measurements.

3.3 Ultrabroadband dye laser

A new method was used to generate ultrabroadband laser pulses from a dye laser with high conversion efficiency and sufficient wavelength stability for the requirements of these experiments. Figure 3.2(a) displays the schematic of the optical configuration for the ultrabroadband dye laser. The ultrabroadband dye laser design was parametrically explored before achieving the desired bandwidth and power output. Key components that were adjusted include the optical cavity geometry, dye choices and concentrations, and a 532 nm pumping strategy for generating a stable, wide-bandwidth, high-energy laser beam centered at \sim 605 nm. For optimal broadband lasing, separate dye mixtures (dye composition and concentration) were used in the two cavity dye cells. Initially, the first dye cell contained 100.0 mg/L of Sulforhodamine 640 in methanol, and the second cell contained 118.3 mg/L of Kiton Red 620 in methanol.



Figure 3.2. (a) Schematic of the optical configuration for the ultrabroadband dye laser. The 532 nm beams were first focused by f = +100 mm spherical lenses and then expanded by f = -50 mm cylindrical lenses prior to pumping the dye cells. A f = +750 mm lens was placed after the amplifier to focus the ultrabroadband dye laser pulses. DC 1, dye cell 1; DC 2, dye cell 2. (b) Measured laser spectra from DC 1 and DC 2 when independently operated and pumped at 532 nm. The normalized fluorescence intensity from DC 1 and DC 2 are plotted in red and blue, respectively. The oscillator spectra are also shown in black when DC 1 is not pumped by 532 nm and DC 2 is pumped with energies of 50%, 75%, and 100% of the maximum value.

Sulforhodamine 640 was then progressively mixed in the second dye cell to red- shift the peak emission wavelength to ~597 nm. This dual-cell cavity configuration allowed the fluorescence from each dye cell to be independently analyzed. The red and blue curves shown in figure 3.2(b) represent the spectra produced when each of the dye cells are pumped with the external 532 nm beam and the fluorescence from the neighboring dye cell is blocked, thereby closing off the cavity. The peak emission wavelengths in the first and second dye cells were measured to be ~606 nm and ~597 nm, respectively. Using this two-dye-cell configuration, the ultrabroadband dye laser was found to emit a bimodal spectrum when both cavity dye cells were simultaneously pumped by the external 532 nm beam. However, when the 532 nm pump beam was removed from the first cavity dye cell, so that the Sulforhodamine 640 dye was pumped solely by the fluorescence within the laser cavity (as illustrated in Fig. 2(a), where only the second dye cell was pumped), the desired ultrabroadband emission of approximately uniform intensity between 597–612 nm resulted. This design produced a highpower spectrum with low dye degradation and low spectral noise (i.e., fluctuations of $\pm 5\%$ of the mean in the full width at 10% of the maximum intensity range).



Figure 3.3. Laser spectrum of the ultrabroadband dye laser measured after the amplifier. The Raman Stokes wavelengths of the probed species are labeled on this spectrum to demonstrate that this laser's FWHM of ~15 nm (410 cm^{-1}) was sufficient to detect each of the species of interest. The Raman Stokes wavelengths were calculated according to the Raman transitions for the probed species and the wave mixing requirement that $k_{532} + k_{556} = k_{BBDL} + k_{CARS}$.

Donor-acceptor relationships allow energy to be transferred between neighboring laser dyes. Two energy transfer mechanisms are expected to dominate in the studied ultrabroadband dye laser [104]. The first is radiative energy transfer, where the fluorescence from the donor dye overlaps with the absorption spectra of the acceptor dye and is then emitted at a longer wave- length. The second is Förster-type energy transfer, which is a nonradiative mechanism caused by dipole-dipole interactions. Radiative and/or Förster-type energy transfer could be responsible for the redshift in the second dye cell when Sulforhodamine 640 was added to the initial Kiton Red 620 concentration [99], [104], [105]. Alternatively, only radiative energy transfer is possible between the mixtures in Dye Cell 1 and Dye Cell 2. Without measuring the absorption and fluorescence spectra for the dyes in each individual dye cell, it is difficult to know why only pumping Dye Cell 2 with 532 nm produced the desired ultrabroadband emission spectrum. However, the mechanism is likely related to the manner in which this pumping technique distributes the pump energy between the two dye cells. The black curves shown in Fig. 2(b) represent the emission spectra produced by the oscillator when Dye Cell 1 was not pumped by 532 nm and the Dye Cell 2 pump energy was varied. The oscillator spectrum with 50% pump energy looks very similar to the independently pumped Dye Cell 2 spectrum. As the pump energy is increased to 75%, the oscillator spectrum is bimodal and the influence of both dye cells can be observed. The approximately uniform oscillator spectrum is finally achieved when the pump energy is raised to the maximum value of 700 mJ/pulse. Figure 3.3 displays the obtained ultrabroadband dye laser spectrum, which was measured after the amplifier with a fiber coupled spectrometer (Ocean Optics). This laser beam was centered at ~ 605 nm, it had a FWHM of ~ 15 nm (410) cm^{-1}) and a temporal pulse width of ~10 ns FWHM. The obtained spectral bandwidth was sufficient for keeping the peaks of all of the major combustion species measured by Gallo et al.[100] within the FWHM ~15 nm (410 cm⁻¹) range, although their FWHM ~23 nm (640 cm^{-1}) Stokes beam allowed



Figure 3.4. Normalized sample spectra and the associated theoretical fitting for a lean case ($\phi = 0.50$) at HAB=3 cm. These spectra comprise a single fit to the average of 100 individual sample spectra. Normalized argon spectra, taken both before and after all of the data was acquired, are also shown

more H_2 and C_2H_4 bands to be probed. It is believed that the local peaks/oscillatory structures in the ultrabroadband laser spectrum could be avoided in future work by improving the alignment of the oscillator cavity. In summary, the first dye cell contained 100.0 mg/L of Sulforhodamine 640 in methanol; the second dye cell contained of 110.7 mg/L of Kiton Red 620 and 32.1 mg/L of Sulforhodamine 640 in methanol; and the cylindrical amplifier dye cell contained 37.0 mg/L of Rhodamine 640 in methanol. Although the emitted spectral profile was less sensitive to the amplifier cell geometry and dye concentration, the output energy was sensitive to these parameters. A 3 mm capillary tube dye cell was used to amplify the oscillator energy by a factor of 30, from ~4 mJ/pulse to a total energy output of ~120 mJ/pulse. It should be noted that Sulforhodamine 640, Kiton Red 620, and Rhodamine 640 were used in this experiment because these laser dyes have high conversion efficiency and high wavelength stability. The typical bandwidth of these laser dyes is approximately 6 nm, which is insufficient for WIDECARS. With the approach demonstrated here, it is feasible to generate an ultrabroad bandwidth laser beam using laser dyes with gain profiles that individually are much too narrow for WIDECARS applications. The photostability of the ultrabroadband dye laser is demonstrated in figure 3.4. This figure shows the CARS signal from non-resonant argon, taken both before and after all data were acquired (over 6 hours). Minimal changes were observed in the wavelengths of these spectra during this time interval. The aver- age percent difference in intensity per pixel of the normalized non-resonant argon spectra was~2%per hour.

3.4 WIDECARS Analysis

Theoretical fits to the recorded spectra were computed using the CARSFWSCcode developed by Cutler et al. [101]. CARSFWSC simultaneously calculates the temperature and species mole fractions using subroutines from the Sandia CARSFT code [106]. The Galatry lineshape model was used for H_2 and the Voigt lineshape model was used for each of the remaining species; except C_2H_4 , which does not currently have a theoretical model in CARSFT [100], [101]. CARSFWSC requires many of the same input parameters as CARSFT. A second pump frequency offset of 818.9 cm^{-1} was selected based on the wavenumber difference between the Nd:YAG laser and the narrowband dye laser. Since water comprises the largest percentage of the non-resonant species, a value of $19.74 \times 10^{18} cm^3/(ergamagat)$ was used for the susceptibility of the non-resonant buffer gas, according to the measurements by Magnotti et al. [107]. The measured spectra were pre-processed prior to being analyzed by the fit- ting algorithm. First, a reference background was subtracted to remove the A/D offset of the CCD detector and any stray light contributions to the spectrum. Second, the spectra were normalized by an average non-resonant CARS spectrum taken in argon. This argon normalization removes the signature of the ultrabroadband dye laser from the spectra. Lastly, the square root of the spectra was calculated, as this value is proportional to the molecular susceptibility. Figure 4 also shows a sample spectrum and the corresponding CARSFWSC theoretical fitting. These data were taken at $\phi = 0.50$ and 3 cm above the burner surface. One hundred individual samples were averaged to form this spectrum, and the CARS signal was normalized for display purposes. The aver- age percent error between the fitted theory and this measured spectrum was 5.5% over the wavelength range required to detect CO_2 , CO, H_2 , and N_2 (i.e., 492.6–499.8 nm). However, the close proximity of the O_2 and N_2 spectral peaks made it difficult for the CARSFWSC code to provide accurate estimates of the O_2 mole fraction. This is similar to the problem discussed by Cutler et al. [101], where local interferences were omitted from their fit to avoid errors when fitting other regions. This issue will be corrected in future work by making a slight adjustment to the wavelength of the narrowband dye laser

3.5 Results and Discussion

Figure 3.5 shows a plot of the average temperatures of the fitted spectra at HAB=1 cm, calculated by averaging the results from multiple fits of individual spectra, plotted against the equivalence ratio. Minimal scatter was observed in the individual temperature fits for these cases, as the standard deviation ranged from 1.5%–2.5% of the mean. The $\phi = 0.50$ and $\phi = 2.06$ cases are not shown in Figure 3.5 because these flames were lifted more than 1 cm off the burner surface. Also included in this figure are the ethylene–air McKenna burner results of Gallo et al. [100] and adiabatic flame temperatures calculated by Cantera with GRI 3.0 . It can be seen that the WIDECARS measured temperatures from both studies are much lower than the adiabatic flame temperature for $\phi = 0.7 - 1.7$. This is because the flame stabilizes close to the McKenna burner at these conditions and loses heat to its watercooled surface. However, the WIDECARS measured temperatures approach the adiabatic flame temperature at the extreme lean and rich equivalence ratios (e.g., the % difference from Tad is 0.2% at $\phi = 1.85$). Sutton et al. [108] observed this same phenomenon in their Rayleigh scattering measurements of a propane-air McKenna burner flame. They argued that the lower flame speeds at these extreme equivalence ratios caused the flame to lift and lose less heat to the burner surface. Furthermore, several previous research works $\begin{bmatrix} 108 \\ -110 \end{bmatrix}$ have attributed the dip in



Figure 3.5. Average temperatures of the fitted spectra at HAB = 1 cm plotted versus the equivalence ratio. The adiabatic flame temperature and the McKenna burner results of Gallo et al. [100] are also shown. Error bars represent one standard deviation.

flame temperature at $\phi = \sim 1.2$ (i.e., the % difference from T_{ad} is 21.2%) to an enhanced flame speed that situates the flame closer to the burner surface. This notion that excessive heat loss causes the $\phi = \sim 1.2$ temperature dip is supported by the Sutton et al.[108] data, where this dip eventually disappeared once the air flow rate was sufficiently increased. Their measured flame temperatures then approached the adiabatic calculations, presumably because the flame lifted off the burner surface at all equivalence ratios. Figure 3.5 also shows that the temperatures from this study are typically 100–150 K higher than those of Gallo et al. [100]; however, the trends are similar between the two data sets. This temperature discrepancy is likely related to the stabilization plate located 2 cm above the Gallo et al. [100] burner and/or the higher air flow rate used in the present work. The stabilization plate is potentially a source for additional heat losses and it reduces the flame's propensity to lift off the burner surface, both of which can lead to the observed effect. Therefore, caution

should be used when comparing these values because it is difficult to isolate the effect of heat transfer to the burner on the temperature measurements. The adiabatic flame temperature calculations and Gallo et al. [100] results are only shown for the purpose of making qualitative comparisons. WIDECARS measured mole fractions are less sensitive to heat transfer to the burner, and therefore chemical equilibrium calculations are a good standard for the accuracy of these measurements [109]. Figure 3.6 shows the average mole fraction ratios of CO_2 , CO, and H_2 with N_2 , at HAB = 1 cm, plot- ted against the equivalence ratio. Good agreement was seen between these average species mole fraction fits and Cantera chemical equilibrium calculations with GRI 3.0. While CARSFWSC determines temperature according to the shape of the fitted spectrum, the species concentrations are based on the ratio of the CARS signal intensity for each species to that of the non-resonant buffer gas [100]. Since the susceptibility of the non-resonant buffer gas includes species other than water and changes with operating conditions, the constant value of $19.74 \times 10^{18} cm^3/(erg \text{ amagat})$ that was specified introduces errors in the calculated absolute mole fractions. Therefore, the concentration fits were presented as mole fraction ratios with N_2 in order to correct for the influence of the unknown non-resonant buffer gas susceptibility.



Figure 3.6. Ratios of the CO_2 , CO, $andH_2$ mole fraction with the N2 mole fraction, plotted against the equivalence ratio. The chemical equilibrium calculations are also shown for each case. These measurements were taken at 1 cm above the burner surface. Error bars represent 1 standard deviation. of

For almost all of the cases, the fitted mole fraction ratios match the chemical equilibrium calculations within the experimental uncertainty. When the measured species had signal-to-noise ratios (S/N) greater than 5 (i.e., all shown in Fig. 3.6 except χCO_2 at $\phi > 1.5$ and χ CO at $\phi = 1.2$), the percent difference between the mole fraction ratio fits and the chemical equilibrium calculations ranged from 2.8%–25.8% (15.0%–45.2% when S/N < 5), while the standard deviation of the mole fraction ratio fits ranged from 5.6%–16.2% of the mean (12.3%–34.0% when S/N < 5).

These temperature and species concentration measurements provided evidence of soot production in this flame at an equivalence ratio of $\phi = 2.06$. Figure 3.7 shows two spectra at this condition with the theoretical fits overlaid, one at HAB= 2 cm and the other at HAB = 4 cm. For the HAB = 2 cm case, it is clear that the flame reaction zone is upstream of the measurement location, as there is no evidence of remaining reactants and the excess fuel has broken down to CO and H_2 . As the flame progresses downstream to HAB = 4 cm, the H_2 and CO mole fractions decrease and a new peak emerges that is highlighted by a dashed red box in the bottom left corner of the plot. Attempts to fit this structure using CARSFWSC found that it was close to, but not coincident with, the theoretical O_2 peak (not shown, see figure 3.4 for an O_2 fitting). Kearney and Jackson [103] investigated the effects of coherent C_2 interference on the spectra of dual-pump CARS measurements taken in sooting flames. They observed a CARS spectrum that was very similar to the one shown in Fig. 7 when the narrowband dye laser was tuned to a wavelength of556.8 nm. Kearney and Jackson [103] saw a peak in their spectrum at 491.6 nm, which they argued was caused by coherent Raman processes in C_2 or other olefinic hydrocarbon species. They also observed features similar to the ripples in the HAB = 4 cm spectrum between 494–499 nm in figure 3.7. Although the source of these features is unknown, they may be caused by absorption from Raman coherent C_2 [70],34].Neither these spectral ripples nor the emergent C_2 peaks were observed in any of the cases with lower equivalence ratios. This is also consistent with the work by Kearney and Jackson [103], as they did not see significant C_2 interference for their ethylene–air McKenna burner flame until $\phi = 2.3$. Interestingly, the average measured



Figure 3.7. Average spectra and theoretical fittings for the = 2.06 flames at HAB=2 cm and HAB=4 cm.

flame temperature decreased more between HAB = 3 cm to HAB = 4 cm for the ϕ = 2.06 flames, whose CARS spectra are shown in figure 3.7, than for the other rich cases. However, the cause of this temperature drop is unknown because a change in the flame length, increased flame flickering frequency, and the possibility of soot enhancing the heat lost by radiation could all be contributing factors. The temperature and species concentration measurements that are made possible by this technique can help supplement what is currently known about reacting flows. For example, WIDECARS measurements have the potential to illuminate key details relating to turbulent flame physics and flame stabilization. The role of turbulence on the flame thickness, preheat zone, and reaction zone composition could be characterized if these measurements were available from a controlled experiment in a turbulent flame. Furthermore, measurements of the temperature and major species concentrations at different locations in a flame near lean blowout would highlight regions of significance for flame stabilization. As there is currently no scientific consensus about what ultimately causes flames to blow out, these measurements would have tremendous value for the combustion community.

3.6 Conclusion

WIDECARS measurements were demonstrated using an ultrabroadband dye laser with a more stable wavelength and power output compared to previously used Pyrromethene- dyesbased lasers. This measurement technique reduced the dye degradation that has impacted previous WIDECARS studies by using a series of traditional, narrowband, stable dyes and a unique pumping strategy for the ultrabroadband dye laser. The ultrabroadband dye laser had a FWHM of~15 nm (410 cm^{-1}), achieved energy outputs up to 120 mJ/pulse, and only fluctuated ±5% of the mean in the full width at 10% of the maximum intensity range. The CARS spectra produced by non-resonant argon further demonstrated the photostability of this system, as their average variation in intensity per pixel was ~2% per hour. The temperature and mole fractions of CO_2 , CO, H_2 , and N_2 in an ethylene–air McKenna burner flame were determined using these WIDECARS measurements. Accurate measurements resulted, and there was no significant difference between the data and theoretical fits by
the CARSFWSC code. The measured flame temperatures were found to be consistent with those taken by other authors using the same fuel and burner configuration. Furthermore, the mole fraction ratios of the measured species with N_2 ranged from 2.8%–25.8% of the chemical equilibrium solutions for cases with acceptable signal-to-noise ratios, which was within experimental uncertainty. C_2 appeared in the spectra for the richest test case (i.e., ϕ = 2.06) and it increased in CARS signal intensity as the measurement location was moved further downstream of the burner surface.

Part II

ADVANCEMENT OF CARS FOR APPLIED HIGH SPEED FLOW MEASUREMENTS

4. BACKGROUND

This chapter covers the advances in CARS as a high-speed temperature measurement for aplied flow environments. The approach taken has been to use burst-mode picosecond CARS to achieve 100 kHz and higher measurements in applied environments, starting from laboratory flames, to energetic material deflagrative events, high temperature plasmas, and even a high enthalpy schock tube. The major advances required to obtain these measurements and make a high speed CARS technique feasible in difficult environments have been 1) building a burst-mode pump CARS instrument with sufficient energy and intensity for the CARS measurements; 2) implementing nonresonant referencing and error-reduction techniques which allowed the measurements performed to provide useful temperature measurements with an acceptable uncertainty, and 3) developing a picosecond CARS specific model that also ensured precision in the measurement. These three aspects are detailed in the following sections, starting with the modeling, as this fits well with the CARS theory, and then the implementation of the measurement is shown in the later sections. Finally suggestions for improvements beyond 100 kHz and beyond ps-CARS are provided with solutions for better measurement quality and speed.

4.1 Burst-mode lasers for CARS

High speed measurements would not be possible without the use of burst-mode lasers, as these are able to provide large amounts of energy at extremely high repetition rates. A very thorough and recent overview of the burst-mode laser can be found in the review by Slipchenko, Meyer and Roy [111]. The burst-mode laser technology was really developed in the last 10-15 years, from short bursts with nanosecond pulses in the early 2000s (cite) to many improvements possible by the R&D at Spectral Energies llc. Now, burst-mode lasers have seen use for imaging, PIV, PTV, PLIF, Schlieren, holography, absorption, Rayleigh scattering, and tomography at rates as high as 5 MHz, and possible J/pulse energies, depending on the application, all with ~1-100 ns pulse widths[34], [42]–[44], [83], [112]–[118]. In the last 5-7 years tests with different pulse widths have provided higher intensities. Amplification of picosecond, and femtosecond pulses is another challenge, which has been overcome

to perform PLEET, FLEET, and CARS. While femtosecond amplification will still require improvements, picosecond pulses can still be amplified with the Nd:YAG laser. Multiple ps burst-mode lasers have been made and sold by Spectral energies llc, with 50-100 ps pulse widths, and 150-200 mJ, 100 kHz 1064 nm pulses. Use of this kind of laser has made possible the measurements described below.

4.2 Solid state parametric optical processes

For single shot CARS measurements a broadband stokes and/or pump beam are necessary. In nanosecond CARS this pulse has been usually generated using dye lasers, as shown in the WIDECARS experiments in the previous section. In femtosecond CARS techniques, instead, the short pulses already have the bandwidth necessary to cover enough transitions for temperature diagnostics. In the picosecond regime, instead, the broadband has been generated with either a modeless dye laser [66], [119], [120], or by parametric processes [121]. At high repetition rates dye depletion makes it unfeasible to use a dye laser, so parametric processes are used.

Parametric optical processes leverage the second order χ^2 nonlinearity in birefringent materials and crystals. Parametric is indicative of the fact that some f the properties of the incident wave are changed. In this process the input photon is coverted into a new photon pair with the same combined energy. This pair of entangled photons is then arbitrarily called signal and idler, where the signal is generally labelled as the photon carrying more energy than the idler. This process is commonly used to produce and measure quantum entanglement states[122]. Figure 4.1 shows the processes of optical parametric generation (OPG) and optical parametric amplification (OPA) respectively. In OPG an input photon is split into two output photons, depending on the phase matching condition, which is determined by the angle or temperature of the crystal. This generation process can also be thought of as an amplification process, as there are many photons in the quantum background (or ambient room) which will match the wavelength and angle of interest, so the pump can be though of as amplifying one of these states. In optical parametric amplification we provide the signal (or idler) photons, which will be strong enough to provide a forcing function to the pump; which effectively means that the threshold for generating (amplifying) signal and idler photons is much lower; there is an phase matching condition where the process will be most efficient. Use of an OPG and OPA system have been shown to provide conversion efficiencies of the pump beam of up to $\sim 25\%$ and OPAs can provide thousands of times amplification with the advantage of minimal absorption [123]–[132] making it a great method to use for high energy and high repetition rate applications, as is the case in the following sections.



Figure 4.1. Representative process of a) optical parametric generation and b) optical parametric amplification

5. PICOSECOND CARS MODELING

5.1 Introduction

Some CARS background was introduced in the front matter of the thesis to give an idea of the processes involved in obtaining the measurements and how these can be made quantitative. Here we will discuss CARS more in depth in relation to measuring temperature, aimed mainly at the use of the commonly measured and most available N_2 molecule, but also applicable to other diatomics such as H_2 and O_2 . The discussion will start with the description of the molecular vibrations, rotations and electronic transitions, the key timescales in CARS, and then specifically look at the approximations made to perform measurements in the nanosecond, and in the femtosecond regimes. Then, the main body of this chapter will discuss contributions to modeling in the picosecond regime.

5.1.1 Quantum mechanical description of molecules

Molecules can be described based on their degrees of freedom and motions allowed. Diatomic, such as N_2 and O_2 are relatively simple because of their D_2V symmetry. These have electronic transitions, vibrational levels, and rotational degrees of freedom, as depicted in figure 5.1, and which have been extensively characterized.



Figure 5.1. Diagrammatic representation of molecular rotational and vibrational energy levels of a diatomic molecule. The shape of the base represents the ground potential of the quantum well

Determination of the energy levels has historically started from simple approximations, upon which added layers have increased the precision of the models. Vibrational level energies are first approximated by a simple harmonic oscillator model, by comparing the diatomic to a mass-spring system connected by a double bond, described by the spring equation : $f(x) = -k\Delta x$ where the force f is proportional to the displacement Δx from an resting equilibrium state, multiplied by a stiffness constant k. The spring-mass description is then introduce into Schrodinger's equation:

$$\frac{d^2\Psi(x)}{dx^2} + \frac{2\mu}{\hbar^2}(E - 0.5kx^2)\Psi(x) = 0$$
(5.1)

From which the vibrational energy levels, at first approximation, are obtained as:

$$E(v) = \hbar v(v+0.5) \tag{5.2}$$

Where v is the vibrational level quantum number. When performing experiments (in the 1970s) it was found that this was a rough approximation. More accurately, the vibrational energy levels are described by anharmonic oscillators as:

$$G(v) = \omega_{\rm e}(v+0.5) - \omega_{\rm e}x_{\rm e}(v+0.5)^2 + \omega_{\rm e}y_{\rm e}(v+0.5)^3 - \omega_{\rm e}z_{\rm e}(v+0.5)^4 + H.O.T.$$
(5.3)

Where the $\omega_e \omega_e x_e, \omega_e y_e$ and so forth have been generally refined with the help of experimental measurements.

On top of the vibrational energy levels, the finer possible rotational energies of the molecule can be described by assuming it is a dumbbell shaped rigid rotating body. Starting with this and plugging into Schrodinger's equation, we get:

$$E(J) = \frac{\hbar^2}{2I} J(J+1)$$
 (5.4)

Where J=0,1,2,3... is the rotational quantum number and I the moment of inertia. This is readily converted into wavenumber units as:

$$F(J) = BJ(J+1) \tag{5.5}$$

Where B is the rotational constant, defined by:

$$B = \frac{\hbar}{4\pi cI} \tag{5.6}$$

For low rotational levels, this is a good approximation, but as the rotational quantum numbers increase, it becomes obvious that the rigid rotor approximation is not valid, as the internuclear distance starts expanding due to centrifugal force, leading to altered energy level location. To accout for this, a small correction term D was added:

$$E(J) = \hbar c [BJ(J+1) - DJ^2(J+1)^2]$$
(5.7)

The next step is to recognize that the vibrational and rotational modes are characteristic of the same molecule, and so are coupled and influence one another. To account for this, B and D now will depend upon the vibrational quantum number as:

$$B_v = B_e - \alpha_e(v + 0.5) + \gamma_e(v + 0.5)^2$$
(5.8)

$$D_v = D_e - \beta_e (v + 0.5) + \delta_e (v + 0.5)^2$$
(5.9)

So the description of each rotational level depends on the vibrational level it lies within, and is characterized as:

$$E_v(J) = \hbar c [(B_e - \alpha_e(v + 0.5) + \gamma_e(v + 0.5)^2)J(J + 1) - (D_e - \beta_e(v + 0.5) + \delta_e(v + 0.5)^2)J^2(J + 1)^2]$$
(5.10)

Noting that the rotational and vibrational energies are coupled, the energy of a specific level must be considered together, so the full description of a ro-vibrational level is described as:

$$E(v, J) = E(v) + E_v(J) = \omega_e(v + 0.5) - \omega_e x_e(v + 0.5)^2 + \omega_e y_e(v + 0.5)^3$$
$$- \omega_e z_e(v + 0.5)^4 + [(B_e - \alpha_e(v + 0.5) + \gamma_e(v + 0.5)^2)J(J + 1)$$
$$- (D_e - \beta_e(v + 0.5) + \delta_e(v + 0.5)^2)J^2(J + 1)^2]$$
(5.11)

This way eq. 5.1.1 quite accurately defines all possible transitions within the ground electronic level of a diatomic molecule. The situation can be much more complicated when the energies in the excited electronic states are considered, especially for larger molecules. Luckily, for most CARS temperature measurements, only the ground electronic state is of interest.

5.1.2 CARS Polarizability

As previously mentioned, CARS signal depends on the induced polarizability change in the molecule. For the gaseous phase, the even ordered polarization terms cancel out (assumption of an isotropic medium) and we are left with odd ordered terms: So, the polarizability is described as:

$$P(\omega_4) = P^{(1)}(\omega_4) + P^{(3)}(\omega_4) + P^{(5)}(\omega_4) + P^{(7)}(\omega_4)...$$
(5.12)

The contribution of polarization terms above 3rd order is trivial in CARS, and only matters in a few techniques. The linear susceptibility of the polarization term, on the other hand is a constant within a medium, defined as:

$$\chi^{(1)} = \frac{\epsilon}{\epsilon_0} - 1 \tag{5.13}$$

So in CARS we are left with $P^{(3)}$, which is defined below, adapted from Eckbreth's laser diagnostics bible [70] as:

$$P^{(3)}(\omega_4) = \epsilon_0 \chi^{(3)}_{ijkl}(\omega_4, \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3)$$
(5.14)

Where $\chi^{(3)}$ is the third order susceptibility, and a summation over j,k,l would be performed; for each of these there are 27 terms, leading to an apparently very complicated result. Thanks to symmetry most of the terms are equivalent; after simplification steps found in [70] one is left with:

$$P^{(3)}(\omega_4) = \epsilon_0 \chi_{CARS}(\omega_4, \omega_1, \omega_2, \omega_3) E(\omega_1) E(\omega_2) E(\omega_3)$$
(5.15)

where the χ_{CARS} represents the remaining terms of the third order susceptibility the complex field is assumed to be of the form:

$$E(\omega_{\rm i}) = E(\omega_{\rm i}) \exp({\rm i}k_{\rm i} \cdot r)$$
(5.16)

5.1.3 Time-independent CARS model

Finally the actual CARS intensity can be written as:

$$I_4 = \frac{\omega_4^2}{n_1 n_2 n_3 c^4 \epsilon_0^2} I_1 I_2 I_3 |\chi_{CARS}|^2 l^2 (\frac{\sin(0.5 \cdot \Delta kl)}{0.5 \cdot \Delta kl})^2$$
(5.17)

Some key take-aways from equation 5.1.3 are: 1) The CARS intensity is linearly dependent with the intensity of each input beam; 2) CARS scales with the square of the absolute value of the susceptibility, which is itself density dependent, so the CARS signal should be expected to scale quadratically with number density (or pressure). The advantage being that at higher pressures a higher signal is expected (this is true only to a certain point), and the downside of this being that because the number density is much reduced at flame temperatures, an integrated signal loss by a factor of at least 70-100 may be expected at 2,000 K compared to room temperature. 3)Technically the CARS signal does not depend on the focal length of the lens used. In experimental practice it is shown that a longer focal length lens produces a longer interaction length a little bit more signal, but the balance between the overlap length and intensity results in small (factor of 2-4) differences as different lens are used. The argument is different for colinear CARS where the interaction length is extremely long.

While the CARS intensity is described here, most temperature measurements are performed independently of the absolute intensity, which is only used as a guideline to estimate whether enough SNR will be attained. In actual modeling and data fitting, the result is normalized, and constants may be left out, or as their purpose is voided by the normalization step.

Until recently CARS was performed in the nanosecond regime, where the time of the pulses is 100s of times longer than the rotational and vibrational dephasing times (10s ps). This means that the measured intensity, described by eq. 5.1.3 represents a time average over 100s of successive excitations de-excitations withing the time of the pulse (involving number of molecules of many orders of magnitude).

For use in spectral modeling, as the Sandia CARSFT [106] code, eq. 5.1.3 is re-written as described by Yuratich et al. [26]:

$$I_4 = K \int |\chi_{CARS}(\omega_1 - \omega_2)|^2 I_1(\omega_1) I_1(\omega_2) I_3(\omega_3) \times \delta(\omega_1 + \omega_2 - \omega_3 - \omega_4) d\omega_1 d\omega_2 d\omega_3$$
(5.18)

Additionally to this description, the Sandia CARSFT modeling software [106] also includes the contribution of the nonresonant background, modeled as a broadband contribution, which depends on density and composition of the probe volume. Also, from this equation it should be noted that the bandwidth of the pump-stokes forcing is assumed to be infinite, so to match the model, the standard approach is to divide the experimental spectra by the averaged measured nonresonant from Argon, or some other dense material such as glass.

5.1.4 Time-resolved CARS model

With the advent of Ti:Sapphire femtosecond lasers, it was possible to produce pulses with lower energies, but orders of magnitude higher intensities, clearly a strong advantage for CARS. The drawback to applying this to CARS, though is that femtosecond pulses are broadband, to the spectral resolution would suffer greatly. To overcome this, either the probe pulse is scanned in time (fs-time-resolved CARS) for multiplex detection, or a picosecond narrowband probe pulse is used (hybrid fs/ps CARS) or the probe is chirped (chirped pulse fs CARS). In all these cases, it is imperative to treat the process as a time-dependent as the pulses are shorter than the dephasing time of the molecule, well detailed in [62].

$$P(t,\tau_{12},\tau_{23}) = (\frac{i}{\hbar})^3 \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_2 \int_{-\infty}^{\infty} dt_1 [R_4(t_3,t_2,t_1) \times E_3(t-t_3) \\ E_2^*(t+\tau_{23}-t_3-t_2) \times E_1(t+\tau_{23}+\tau_{12}-t_3-t_2-t_1) \\ \times e^{i(\omega_1-\omega_2+\omega_3)t_3} e^{i(\omega_1-\omega_2)t_2} e^{i\omega_1t_1}]$$
(5.19)

Here t_1, t_2, t_3 are the pulse durations and τ_s the delays between the pulses, P is the third order polarization, R4 is the molecular response, and the recorded CARS intensity is $|P|^2$ For most measurements using femtosecond lasers, the excitation pulses E_1E_2 are assumed to be time-coincident (the same beam in the experiment) and approximated as a delta function, so that the equation is vastly simplified to:

$$P(t,\tau_{23}) = \sqrt{I_1 I_2} (\frac{i}{\hbar})^3 \int_{-\tau_{23}}^{\infty} dt [R_4 \times E_3(t-t_3) \times e^{i(\omega_1 - \omega_2 + \omega_3)t}]$$
(5.20)

Or, as best described by Stauffer et al. [62] in terms of the vibrational transition c-a and the dephasing constant $\Gamma_c a$, and leaving out some trivial constants:

$$P_{CARS}(\Delta,\tau_{23}) = (\frac{i}{\hbar})^3 e^{i(\omega_1 - \omega_2)\tau_{23}} \times \int_{-\tau_{23}}^{\infty} dt E_3(t) s^{i(\omega_1 - \omega_2 + \Delta)t} \times \sum_{a,c} I_{ca} e^{(i\omega_{ca} - \Gamma_{ca})(t + \tau_{23})}$$
(5.21)

Where Δ is the frequency detuning compared to the CARS signal. Note that the intrinsic result of assuming that the preparation pulses are delta functions leads to infinite bandwidth of these pulses. In most experiments the bandwidth is 100-300 cm⁻¹ and does result in a much different looking spectrum. This can be changed by either adding gaussian pulses in the frequency domain after an FFT from the time-response is performed, or, more simply, the result can be multiplied by the nonresonant background Argon measurement (akin to what is done for CARSFT) for the comparison to the experimental data. The simplified time domain approach has been widely implemented into hybrid fs/ps CARS experiments in many environments using the Ti:Sapphire and either a 10 Hz picosecond laser, a pulse shaper, or a narrowband amplifier to obtain kHz rate measurements.

5.2 Modeling approach for the picosecond pulse regime

5.2.1 The picosecond regime in gas-phase diagnostics

In the previous sections we have described the nanosecond and the femtosecond regimes. The former is modeled as a time-averaged result, while the later is at the opposite end where the excitation can be modeled as a delta function. In the picosecond regime, neither of those approximations are realistic, because the 100 ps pulses used are on the order of \sim 1-4 times the dephasing time, depending on the molecule and transition of interest.

5.2.2 Incoherent sum approach

For this reason, an approach unique to ps-CARS needs to be taken to correctly model and be consistent with the experimental results. The approach to be used needs to be accurate, and straightforward to implement in an experiment, so it should not be overly computationally intensive, and also should not require extremely precise characterization of the laser system output characteristics, an aspect which has severely limited techniques such as chirped probe fs-CARS to fundamental, extremely controlled environments. One approach that could be taken is to use the full time-domain computation, yet this is both computationally intensive, and requires the knowledge of too many pulse characteristics (shape, chirp parameters, phase, ecc...) which may be varied even just by adding a window, when the whole purpose of high speed picosecond CARS measurements is to be able to work in challenging environments.

After testing different approaches, I came up with the idea of using a model that is simple and fast, and which can be adapted to the picosecond regime. The first attempt there was to simply take the impulsive femtosecond model and perform a summation that would result in getting picosecond duration excitations. When I tried this, the result was useless: the various excitations decaying summed destructively and did not produce any sensible spectra. The solution to this was to sum the absolute value of the excitations. While I had no strong backing for this, it did provide the results I was looking for, and I successfully tested this incoherent summation method with experimental data collected. Later, digging into literature I found that there was some theoretical backing to this approach. While I could get the correct equation for modeling, and tried , it was Sean Kearney who was able to do the strict derivation which mathematically backs the use of this method, even though it already seemed effective when used to fit experimental data. The derivation, and further model validation are shown below. It should be noted that the mathematical derivation is required, but not sufficient, as the experimental validation is equally important to show that a mathematically self-consistent model is true in the physical world.

5.2.3 Incoherent sum model derivation

In order to model picosecond CARS, a different approach is taken. The approach consists in performing an incoherent sum over many impulsive response functions, and probing this sum over the whole time history. The derivation for this can be done starting with the expression developed by Stauffer et al.[62] for pulses far from electronic resonance:

$$E_4(t) = E_3(t - \tau_{23}) \int_{-\infty}^{\infty} E_1(t_1) E_2^*(t_1 - \tau_{12}) \chi(t - t_1) e^{i(\omega_1 - \omega_2)t_1} dt_1$$
(5.22)

Where indices 1,2,3,4 refer to the pump, stokes, probe, and CARS electric fields respectively, and χ is the molecular response for an impulsive pump/stokes forcing pulse. The detected CARS spectrum intensity $I_4(\omega)$ will be given by the squared magnitude of the Fourier transform (eq. 5.23) of eq.(5.22)

$$F\{E_4\} = \int_{-\infty}^{\infty} E_3(t-\tau_{23}) \mathrm{e}^{-\mathrm{i}\omega t} \int_{-\infty}^{\infty} E_1(t_1) E_2^*(t_1-\tau_{12}) \chi(t-t_1) \mathrm{e}^{\mathrm{i}(\omega_1-\omega_2)t_1} dt_1 dt \qquad (5.23)$$

From which we obtain the CARS intensity I_4 :

$$I_{4}(\omega) = F\{E_{4}\}F^{*}\{E_{4}^{*}\} =$$

$$\int_{-\infty}^{\infty} E_{3}(t-\tau_{23})e^{i\omega t} \int_{-\infty}^{\infty} E_{1}(t_{1})E_{2}^{*}(t_{1}-\tau_{12})\chi(t-t_{1})e^{i(\omega_{1}-\omega_{2})t_{1}}dt_{1}dt \qquad (5.24)$$

$$\int_{-\infty}^{\infty} E_{3}^{*}(s-\tau_{23})e^{i\omega s} \int_{-\infty}^{\infty} E_{1}^{*}(s_{1})E_{2}(s_{1}-\tau_{12})\chi^{*}(s-s_{1})e^{-i(\omega_{1}-\omega_{2})s_{1}}ds_{1}ds$$

Note that the Fourier transform of the complex conjugate is defined as: $G^*(\omega) = F^*\{g^*(t)\}$ where G is the Fourier transform of g It may also be noted that when the fourier transform is taken, we are "stuck" with a mix of time and frequency variables, with $s = t - \tau$. The key is to somehow separate the time and the frequency components. Now, for ps-CARS the stokes pulse is broadband, is modeled as a statistically phase averaged random fixed bandwidth pulse, and can be written as

$$E_2(t) = \tilde{E}_2(t)f(t)$$

$$< \tilde{E}_2\tilde{E}_2^* >= I_2(t$$
(5.25)

where f is a statistically stationary random process, so that:

$$\langle f(t) \rangle = 0$$
 $\langle f(t)f(s) \rangle = 0$ $\langle f(t)f^{*}(s) \rangle = \phi(t-s)$ (5.26)

Where ϕ represents the auto-correlation function of f, and $s = t - \tau$ Using the above, the spectral intensity can now be re-organized as:

$$< I_{4}(\omega) > = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_{1}(t_{1}) E_{1}^{*}(s_{1}) \tilde{E}_{2}^{*}(t_{1} - \tau_{12}) \tilde{E}_{2}(s_{1} - \tau_{12}) E_{3}(t - \tau_{23}) e^{-i\omega t}$$
$$\chi(t - t_{1}) e^{i(\omega_{1} - \omega_{2})t_{1}} E_{3}^{*}(s - \tau_{23}) e^{i\omega t} \chi^{*}(s - s_{1}) e^{-i(\omega_{1} - \omega_{2})s_{1}} \phi(t_{1} - s_{1}) dt \, ds \, dt_{1} \, ds_{1}$$
(5.27)

Equation (5.27) is further simplified by noting that to obtain bandwidth for the experiments, the picosecond stokes pulse has a low-coherence time (< 130*fs*) pulse compared to the rotational level relaxation time, so $\phi(t_1 - s_1) \rightarrow \delta(t_1 - s_1)$, and integration over s_1 is trivial, and $I_n(t) = E_n(t)E_n^*(t)$ which gives:

$$< I_{4}(\omega) > = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I_{1}(t_{1}) I_{2}(t_{1} - \tau_{12}) E_{3}(t - \tau_{23}) e^{-i\omega t} \chi(t - t_{1}) e^{i(\omega_{1} - \omega_{2})t_{1}} E_{3}^{*}(s - \tau_{23}) e^{i\omega t} \chi(s - s_{1}) e^{-i(\omega_{1} - \omega_{2})s_{1}} \delta(t_{1} - s_{1}) dt \, ds \, dt_{1} \, ds_{1}$$
(5.28)

Then we integrate over s_1

$$< I_{4}(\omega) > = 1 \times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I_{1}(t_{1}) I_{2}(t_{1} - \tau_{12}) E_{3}(t - \tau_{23}) e^{-i\omega t} \chi(t - t_{1}) e^{i(\omega_{1} - \omega_{2})t_{1}} E_{3}^{*}(s - \tau_{23}) e^{i\omega t} \chi(s - s_{1}) e^{-i(\omega_{1} - \omega_{2})s_{1}} dt \, ds \, dt_{1}$$
(5.29)

And re-organizing the integrals:

$$< I_{4}(\omega) > = \int_{-\infty}^{\infty} \left[I_{1}(t_{1}) I_{2}(t_{1} - \tau_{12}) \int_{-\infty}^{\infty} E_{3}(t - \tau_{23}) \chi(t - t_{1}) \mathrm{e}^{\mathrm{i}(\omega_{1} - \omega_{2})t_{1}} \mathrm{e}^{-\mathrm{i}\omega t} dt \right]$$

$$\int_{-\infty}^{\infty} E_{3}^{*} \chi(s - s_{1})(s - \tau_{23}) \mathrm{e}^{-\mathrm{i}(\omega_{1} - \omega_{2})s_{1}} \mathrm{e}^{\mathrm{i}\omega t} ds dt_{1}$$
(5.30)

Where the 2nd and 3rd terms in the integrals are the CARS electric field and conjugate:

$$E_4(\omega, t_1, \tau_{23}) = \int_{-\infty}^{\infty} E_3(t - \tau_{23})\chi(t - t_1)e^{i(\omega_1 - \omega_2)t_1}e^{-i\omega t}dt$$

$$E_4^*(\omega, t_1, \tau_{23}) = \int_{-\infty}^{\infty} E_3^*(s - \tau_{23})\chi^*(s - s_1)e^{-i(\omega_1 - \omega_2)s_1}e^{i\omega t}ds$$
(5.31)

So that substituting 5.31 into 5.30

$$\langle I_4(\omega) \rangle = \int_{-\infty}^{\infty} I_1(t_1) I_2(t_1 - \tau_{12}) E_4(\omega, t_1, \tau_{23}) E_4^*(\omega, t_1, \tau_{23}) dt_1$$
(5.32)

Let us denote a correlation function $G(\omega, t_1, \tau_{23}) = E_4 E_4^*$ so that finally:

$$\langle I_4(\omega) \rangle = \int_{-\infty}^{\infty} I_1(t_1) I_2(t_1 - \tau_{12}) G(\omega, t_1, \tau_{23}) dt_1$$
 (5.33)

Note that τ_{12} is the measured pump-stokes delay, and the integral is taken over all time-steps. The CARS response function remains the same over each time step, but is probed (in the correlation function) at different delays, and then effectively multiplied by the pump-stokes intensity for each time-step.

In the short impulsive limit convergence to the hybrid femtosecond/picosecond CARS approach is met when $I_1I_2 \rightarrow \delta(t - t_1)$ where the convergence to a delta function is relative to the molecular dephasing time of 10-100 ps. The limit is expected to be met for pulses on the order of < 500 fs, and is verified in a following section.

In the long time-domain the use of a long probe pulse is expected to be in agreement with the time-independent computational approaches such as the Sandia CARSFT code, because we started with the same equation, and going to the long time domain results in effectively averaging over the dephasing times. Further considerations can be made on the noise characteristics of the stokes pulse, which can also have a strong influence on the outgoing CARS spectra. This aspect is detailed in a later section.

5.2.4 Ro-Vibrational CARS: Q-Branch

To compare to the available flame temperature experimental data, focus is first put onto the ro-vibrational Q-Branch of Nitrogen. The susceptibility of the Q-branch can be described as:

$$\chi(t) = \sum_{v,j} \Delta N_{v,j} \left(\frac{d\sigma}{d\Omega}\right) \cos(\omega_{v,j}t) \exp(-\Gamma_j t)$$
(5.34)

Where the summation is over the vibrational and rotational quantum numbers, ΔN the population difference with Raman strength $(\frac{d\sigma}{d\Omega})$ and Γ are the collisional Raman line-widths.

In particular, the Q-branch is characterized by the $[\nu \rightarrow \nu + 1]$ vibrational transition; so that we only consider the transition frequencies $\omega = \omega_{\nu+1,J} - \omega_{\nu,J}$. The corresponding transition strengths can also be described as $I_{ca} = I_{\nu+1,J\leftarrow\nu,J}$ where

$$I_{ca} = \frac{(\nu+1)}{(\omega_{\nu+1,0} - \omega_{\nu,0})} \left(1 - \frac{P_{\nu+1,J}}{P_{\nu,J}}\right) x \left[F_{iso}(J) + \frac{4}{45} b_{J,J} \left(\frac{\gamma}{a}\right)^2 F_{aniso}(J)\right]$$
(5.35)

This expression accounts for the Q-branch N_2 anisotropy, and the constants for the rotational dependent transition coefficients are obtained from [62] and implemented in the models.

The anharmonicity constants from (references), such as $B_{\rm e}$ and $\omega_{\rm e}$ are used to describe the effects of ro-vibrational coupling by:

$$F(J) = 1 - \frac{2B_{\rm e}^2}{\omega_{\rm e}}^2 (J)(J+1)[1.5(a_1+1) - 4\frac{p_2}{p_1}$$
(5.36)

where $\frac{p_2}{p_1}$ is the polarizability ratio corresponding to 0.31 and 0.57 for the isotropic and the anisotropic parts respectively.

5.2.5 Code implementation

As described in the theoretical considerations in the introduction, it is assumed that the population states follow Boltzmann statistics; and the modified exponential gap model (MEG) with empirical fit variables from [133] is used.

While various theoretical comparisons are typically performed in the ideal situation of zero nonresonant contribution, in some parts of this chapter a non-resonant contribution is implemented as a 90° phase shifted broad lorentzian linewidth corresponding to a short γ decay in the temporal domain. This is described in frequency as:

$$NR(\omega) = \frac{\mathrm{i}}{1 + 4\frac{(\omega - \omega_0)^2}{\Delta\omega^2}} \tag{5.37}$$

Which, fourier transformed into the temporal domain, corresponds to a short decay when $\Delta \omega$ is set to $\sim 1000 cm^{-1}$



Figure 5.2. Sample steps of the incoherent sum shown with the modeled pulse location in time on the left side, and the running sum on the right, after pump/stokes intensity weighting. Note the trivial influence of the beginning parts, which contribute $\sim 10^{-17}$ to the overall intensity.

Figure 5.2 depicts the process followed by the code. Multiple delays of the impulsive delta function are modeled and then they are added together by a pulse-intensity weighted average. Note that the shape of the spectra changes over the summation, because this corresponds to probing the impulse response at different time delays, with the added necessary weighting factor. While a few sample steps of the summation are show in figure 5.2, the total number of steps varied from $\sim 64,000$ to ~ 100 depending on the delay step of choice.

After the full computation is complete, the result needs to be corrected by the experimental data. In the simulation an infinite bandwidth was given to the pump and stokes pulses, while the probe was modeled in the time domain as bandwidth limited, with the possibility of being changed to a different shape. To match the experiment, the result is multiplied by the nonresonant background taken for a zero time delay in Argon or glass, or other material with only second order susceptibility $\chi^{(2)}$. The procedure is shown in figure 5.3; the change in spectra really depends on how broad the pump/stokes bandwidth is.



Figure 5.3. Left: nonresonant background gaussian fit and spectra for an infinite bandwidth pumping. Right: Infinite pump spectra and corrected spectra results.

Comparison to time-independent model

The incoherent sum model validated through the above mathematical derivations, and implemented for fitting of the experimental data is now compared to the time-independent model generally used for N_2 temperature fitting of nanosecond CARS data, with the use of the Sandia CARSFT software [106]. This modeling approach is valid for pulses which are much longer (~ 10x) the molecular dephasing times. By comparing the results for different pulse durations it is possible to show that the incoherent sum model developed can be also applied in the long pulse limit; while the limitations of the CARSFT model are better defined. The mathematical description of the time-independent model is described in the introduction of this section.



Figure 5.4. Comparison between time-independent CARSFT and Incoherent sum code for different preparation pulse widths. The instrument function was set to $0.5 \ cm^{-1}$ for both, with a modeled temperature of 2,000 K. The Residual shown is the square of the difference between the two curves, shifted down by 0.1 units for clarity.

Figure 5.4 shows the comparison between the developed incoherent sum picosecond model and the Sandia CARSFT model, which is generally used for pulses on the order of $\Delta t > 3ns$. We find that in the short pulse domain the peak intensity of the bands is still comparable, but the shape of the bandhead is very different, as a lot more of the molecules are distributed in the lower rotational states for shorter pulses. At durations of $\sim 3x$ the dephasing time we note that the probability distribution is much broader, while there is still a narrow peak at the bandhead (300 ps pulses). For pulses above 500 ps, the difference is every small and would likely not affect the temperature fitting significantly. We repeat the comparison at lower and higher temperatures of 1,000 and 3,000 Kelvin respectively, then look at the residuals vs temperature for the different pulse widths.



Figure 5.5. Comparison between time-independent CARSFT and Incoherent sum code for different preparation pulse widths. The instrument function was set to $0.5 \ cm^{-1}$ for both, with a modeled temperature of 3,000 K. The Residual shown is the square of the difference between the two curves, shifted down by 0.1 units for clarity.

From 5.5 we see that at 3,000 K the two models appear to converge slightly quicker, as the pulse width increases, compared to the results at 2,000 K in fig. 5.4. The opposite appears to be true for lower temperatures, as in figure 5.6 which models the two at 1,000 K, the bandhead still shows some differences at 1 ns pulse width.



Figure 5.6. Comparison between time-independent CARSFT and Incoherent sum code for different preparation pulse widths. The instrument function was set to $0.5 \ cm^{-1}$ for both, with a modeled temperature of 1,000 K. The Residual shown is the square of the difference between the two curves, shifted down by 0.1 units for clarity.

The cases for 1,000-3,000 K show that the incoherent sum approaches the time-independent simulation at pulses ~ 750 ps, with the approach being quicker at higher temperatures. It may be better to say that the time-independent model is valid for pulses as low as 500-750 ps depending on the temperature of interest.

The pulse-temperature dependence may be better understood by looking at a 2D plot of the residual least squared normalized difference between the two codes.



Figure 5.7. 2D contour plot of residuals for pulse widths and temperatures when comparing CARSFT to the picosecond incoherent sum.

To obtain figure 5.7 simulations were performed at 200 K intervals and 50 ps pulse width intervals with both models, and then compared by obtaining the residual and normalizing it by the picosecond result integrated area for consistency between different temperatures. The results show that, as already noted in the sample spectra, for pulses below 300-400 ps CARSFT is quite different from the picosecond calculation. For higher temperatures this restriction is slightly relaxed, but for lower temperatures, the differences are present up to higher pulse widths, and only around 3-10 ns do spectra at T < 500K match the timeindependent calculation.

This defines that for quick fitting CARSFT could be used for ps-CARS at > 2,000K with pulses ~ 300 ps, but should be avoided for lower temperatures.

Comparison to the impulsive model

As the incoherent sum model was expected to converge with the time-independent model for long pulse durations, in the pump/stokes delta function limit, this is expected to be in agreement with the model for hybrid femtosecond/picosecond CARS if it is to be used as a mode general approach valid in multiple experiments.

The main difference between the two models is that the impulsive pump/stokes excitation which is used as an approximation in the hybrid fs/ps approach; is repeated for every Δt through an incoherent sum, resulting in the summations of many impulse-response functions weighted by the pulse shape.

Because of this, the main differences between the two codes are found in the regimes where the collisional dephasing is nontrivial. These correspond to the cases of 1) overlap between the pulses (0-10 ps probe delay), 2) lower pressures where the collisional quenching is low enough to have an effect for a short enough probe delay. For significant probe delays, the still noticeable difference is that with the impulsive code, while the experimental spectra can still be nicely fit, the best-fit probe delay is shorter than the actual measured pulse delay, which can cause varying temperature fitting offsets due to a different modeling of the J-level exponential decay, given that molecules in the highest J-levels are the slowest tot decay to the ground state.

For a case similar to experiment, with 100 ps probe pulses, the difference is most significant for zero delay ($\tau_p = 0$), with the residual falling off at $\sim \tau_p = 0.5t_p$, and an almost perfect match at $\tau_p = 2t_p$ as shown in figure 5.8



Figure 5.8. Comparison between impulsive and incoherent sum models at varying delays. The instrument function is $1 \ cm^{-1}$ and the stokes pulse is 66 ps at FWHM, equilibrium temperature is set to 2,000 K

The residual integrated over the whole range of interest, versus delay is shown in figure 5.9. As the delay is increased, the number of molecules in the excited state decays, leading to a reduced signal. For this reason, the residual was normalized by the area (or integrated CARS signal). As noted, the residual falls off to $\frac{1}{2}$ of the initial value by $\sim \tau_p = 0.5t_p$ and to $\sim \frac{1}{e^2}$ by $\tau_p = 0.5t_p$.



Figure 5.9. Normalized residuals versus delay for the 100 ps probe case.

Similar results are also found when a 50 ps probe pulse is used. As noted before, the use of an effective delay for the impulsive model can improve the fit. In order to do this, the delay was optimized by creating the simulated spectra with the picosecond incoherent sum model, then fitting these with the probe delay as a free variable at the zero time delay step of the picosecond code. The best effective delay for that particular case is found to be 11 ps, but this is expected to vary depending on the temperature and on the effective delay because of the change in averaged dephasing time at different temperatures.



Figure 5.10. Left: comparison between impulsive and ps for the same probe delay. Right: Same conditions, with an 11 ps probe delay added at every step of the impulsive calculation

After seeing these results one might think that the quickest way to perform the modeling is to add an effective delay to the impulsive calculation, as it appears that the match between the two is then fairly close once the delay is set. The challenge with this approach is that the effective delay varies with temperature, as is shown in figure 5.11. At a higher temperature a longer effective delay is necessary for fitting the time zero calculation, and in both cases the residual shows that there still are significant differences if only the delay is changed, so the issue is mitigated by giving a much better fit compared to the ones shown on the left pane of figure 5.10, but not solved.



Figure 5.11. Sample spectra for two different temperatures, fit with the effective delay method, to the time zero incoherent sum picosecond calculation. At 2,000 K an effective delay of 11 ps is best, while at 3,000 K the best effective delay is

Comparison to experimental data

An important aspect of the model validation is the comparison to the experimental data. While the model results self-relevant due to the consistency of the mathematical derivation, it is always possible that experimental aspects have been neglected. Case in point is the nonresonant background, which is an essential part to ensure that the model is true to the experiment in picosecond CARS, but was not necessary in the theoretical comparison to the impulsive and the time-independent models.

The experimental data used for this final model validation step is two-fold. The first data-set is from 100 kHz CARS calibration measurements in a Hencken burner, for the validation to this data I refer the reader to figure 6.5 in the 100 kHz demonstration chapter. In this section we look at data from averaged 10 Hz picosecond CARS measurements, kindly provided by Hans Stauffer and Paul Hsu who took the data in 2015 for a separate measurement campaign. Two useful data sets were provided: the first is nitrogen in a nonreacting oven at 900K, where the probe delay was varied from 0 to 200ps, letting us compare the

validity of the model over a large range of delays. The second data set is in a Hencken burner with an H_2/air mixture at $\phi = 0.3 - \phi = 1.0$.

Below we show the fits with the picosecond model for the different phi's. The delay, temperature, instrument function, and nonresonant background were allowed to vary. From the results we find that the fits are within less than 20 K compared to the adiabatic flame temperature. It should be noted that the actual temperature is expected to be very close to the adiabatic due to the use of a Hencken burner, and due to the fact that the measurements are averaged over 1,0000 pulses. For comparison, fitting is also performed using the impulsive model with a variable, optimized delay.



Figure 5.12. Model fits to experiment from H_2/air data with different equivalent ratios. The data is a result of 1,000 shot average from 3 beam Box-CARS and ~200 ps delay

For reference, figure 5.13 shows the 2D optimization space for temperature and probe delay of the $\phi = 1$ condition. It appears that the fitting is more sensitive to temperature than to delay, and the expectation would be that even if there is some fitting ambiguity in the delay, the temperature fitting ambiguity would be lower.



Figure 5.13. Example from model fitting showing the 2D residual map for temperature and probe delay for the $\phi = 1$ condition

Computational efficiency

The impulsive computation is performed with a step size of 9 fs, which was determined by Nyquist. When the calculation is repeated over all time delays the smallest delay time step can be 9 fs. Taking the picosecond calculation with the 9 fs time-step as the ground truth, the full picosecond calculation was performed with increasing step size. At a 9 fs step size, the impulsive calculation is performed $\sim 32,000$ times (32,218), which takes slightly less than 2 minutes (110 seconds). With a larger step size the computation time is much shorter. The select step size is of 702 fs, which takes 2 s per spectra versus the impulsive calculation which takes 0.8 s per spectra. At 702 fs time step ~ 415 impulsive calculations are made, but the code only takes 2.5 times what it takes for an impulsive code run as a significant amount of the computational time in the impulsive calculation is in the variable initiation rather than the actual CARS spectra calculation. The sum residual at a step of 702 fs is of $6.410^{-5}\%$ when compared to the "ground truth" of the full incoherent sum calculation. Use of an incoherent sum reduced computation allows to still model the CARS process more accurately while limiting the increase in computational time.



Figure 5.14. Characterization of the computational time and residual for different step sizes in the picosecond incoherent sum model at zero time delay

As shown in figure 5.14 the optimal step size to use was determined for a zero probe time delay. This is because it was found that for longer probe delays, the residual (normalized by the total signal) is much lower, and remains below the time-zero residual even for large step sizes, as shown in figure 5.15. Selection of the time-step to use for the incoherent sum calculation could be varied depending on the computational availability. Use of the smallest step size will provide the most accurate model, but the difference is trivial up to the currently selected step size.



Figure 5.15. Characterization of the computational time and residual for different step sizes in the picosecond incoherent sum model at longer time delays

We can conclude that while the incoherent sum calculation will remain longer than the impulsive one, the "sweet spot" of \sim 700 fs step size results in a .5 time loss in computational time, which is deemed acceptable sacrifice, considering the return in accuracy compared to the impulsive model. CARSFT here is not even considered because it is much slower, and I have not tested the potentially faster batch version of the FORTRAN CARSFT code. Another important note on the computational time is that these calculations were all performed with a fairly limited Asus Zen laptop computer with 8 Gigabytes of RAM and a CPU of four cores at a speed of 1.8 GHz, which resulted in hour long computations when scanning over many free variables. Use of a higher performance computer could definitely improve overall computational time, and the incoherent sum is a perfect setup for parallelization, which may further reduce the computation time gap between the two models.

5.2.6 Rotational CARS

Rotational CARS model

Because pure rotational CARS is now commonly used in hybrid fs/ps CARS measurements, and the application of ps-cARS to high-speed S-Branch measurements may be of interest, we also take a look at the models in the S-branch. For the S-branch the same incoherent sum model is used for picosecond CARS. Analysis is made here to determine the conditions at which the different models should be used for a rotational CARS experiment. Rotational CARS is especially useful at lower temperatures due to the high sensitivity of the rotational transitions to Boltzmann distribution, even down to temperatures as low as 50 K, as has been shown in [68].

Comparison to the time-independent model

We first compare the model to the CARSFT time-independent calculation by looking at different temperatures in the long time domain (1 ns) limit, where these are expected to agree



Figure 5.16. Comparison between the ps and the nanosecond CARSFT code in the long time domain (1 ns pulses) regime, shows excellent agreement

From the CARSRFT comparison we find that the agreement in the long time domain, between the two models is excellent. This shows that the constants are valid up to a longer time domain, so the rotational model could be used even for nanosecond measurements if necessary. The next step is to compare the models at different pulse widths and temperatures. As CARSFT is time-independent, the outcome is always the same, while the picosecond model will vary appropriately. We show below the fits for 2,000 K and for 300 K, as many applications of interest for rotational CARS would be closer to room temperature.



Figure 5.17. Comparison between the ps and the nanosecond CARSFT code at 2000K for decreasing pulse width

From figure 5.17 we note that there are some differences for shorter pulse-widths, but overall the fit is pretty good between the two. The residuals start being obvious only for $t=\sim50$ ps or less, and don't increase drastically even at 1 ps. For the 300 K fits, surprisingly, the spectra match even better than the flame temperature case: here small differences are noticeable really only for t < 10ps.



Figure 5.18. Comparison between the ps and the nanosecond CARSFT code at 300K for decreasing pulse width

A more complete picture of the situation may be provided by a 2D map of the residuals, obtained by varying the pulse widths and temperatures from 300 K to 3,000 K and 1 ps to 1,000 ps respectively.


Figure 5.19. 2D map of the residuals for pulse width and duration, summarizing the results from the previous figures

From the 2D plot we find that for lower temperatures the fit is excellent down to a very short pulse width. At higher temperatures, the fit is less accurate as we approach the 50 ps pulse width. Compared to the Q-branch fitting, though, the expected temperature error between the two models is much much lower, and the temperature dependent trend is opposite: better fits for lower temperature, worse for higher temperature.

Overall, we may conclude that the difference between the two models at the expected experimental condition of \sim 50-100 ps pulse widths is trivial and the two models could be used almost interchangeably at temperatures below 1,000 K.

Comparison to the impulsive model

In hybrid fs/ps CARS the S-branch is most often used, not only for the low temperature sensitivity, but also for the ability to perform measurements up to 50 bar without need for significantly changing the model parameters [13], as the resonant S-branch decay is relatively insensitive to pressure. The technique is great at low temperatures, the only drawback to

keep in mind for ps-rotational-CARS is that at flame temperatures the bandwidth needed is close to 400-500 cm^{-1} compared to ~120 cm^{-1} being enough for the Q-branch. We first look at comparisons between the impulsive and the incoherent sum model for different pulse-widths. In the Q-branch it was observed that at zero time-delay, there was always a significant difference between the two models, for a 66 ps pump/stokes preparation pulse, so we aim to understand whether this is the case in the S-branch.



Figure 5.20. Fit between the rotational picosecond and the impulsive models for different pulse widths, at Left: 300 K ; and Right: 2000 K

From fig. 5.20 we observe that the impulsive code and the incoherent sum code match very closely for the short pulse durations, which are getting close to the impulsive preparation (pump/stokes) approximation. For pulses above 10 ps, the difference between the physically correct result and the impulsive approximation is noticeable in the increase of the residuals. At 50 ps the difference is rather large. At 100 ps the discrepancy increases even further. We note that the divergence between the two is slightly lower at room temperature, similar to what we observed in the comparison to the time-independent model. The higher error at flame conditions can be attributed to the fact that the higher level J decay is longer than the decay of the lower J numbers, so the higher pumped J-lines cause a larger divergence between the two models.

The next step is to observe the differences at varying delays.



Figure 5.21. Fit between the rotational picosecond and the impulsive models for different pulse delays at a set width of 100 ps and 300 K



Figure 5.22. Fit between the rotational picosecond and the impulsive models for different pulse delays at a set width of 100 ps and 2000 K

Figure 5.21 and 5.22 show the difference between the models for different delays at 300 K and 2,000 K respectively, for a 100 ps pulse. Both show that at no delay there is significant difference, then this is lower and lower up to 50 ps. Then, in the 300 K case, we observe the residual increasing again. A similar result is obtained at 2,000 K, but is less obvious at high temperature. The observed trend may seem confusing until we note that the residual is biased towards higher J numbers: in one model the lower J levels are higher, and in the other one the higher J levels are more populated. This difference is somewhat "cancelled out" in the 20-80 ps range possibly because the pulses are overlapping and the beginning or end of the pulse are not as influential.

On the other hand the results shown in figure 5.23 paint a different story: the residual falls to a minimum around 7-8 ps and then increases again. This apparently differs from the previous figures because it is the absolute value of the residual, so the imbalance between Jlevels is not captured at all. It's also important to note that the 300 K residual was doubled here for visualization purposes.



Figure 5.23. Residual versus delay for the impulsive to ps rotational comparison. Inset shows residuals for short probe delays. The pulse width was set to 100ps for pump/stokes, and the residual at 300 K was multiplied by 2 to show both closer together

The result is that these models do differ significantly not only at time-zero, but also for larger pulse delays, while the match is quite close for pulses ~ 10 ps. This means that the incoherent sum model could (obviously!) be used for hybrid fs/ps CARS data analysis, but the opposite is not true, and it would actually be much better to use the time-independent CARSFT if the picosecond model were not available.

Experimental data comparison

While we would like to compare the model to experimental data, the only available data was again kindly provided by Dr. Paul Hsu. The fitting to the 300 K data is shown below, but two issues are obvious: 1) The nonresonant background falls quickly and is close to the edge; and 2) the data is polluted by Oxygen lines.

From the fit in figure 5.24 it is obvious that some peaks (from O_2) are not captured, and also the uncertainty in the exact position of the nonresonant background added some challenge for the fitting.

The comparison to rotational data may be performed in the future, after implementing O_2 and N_2/O_2 line mixing, as well as obtaining rotational data for broader stokes pulses. Observing this figure we cannot help but note that if the measurement had been of the Q-branch, the shown ~100 cm⁻¹ pump/stokes bandwidth would have been more than sufficient for flame-temperature measurements.



Figure 5.24. Model fit to experiment for room temperature N_2 100-shot average

5.2.7 Conclusion

A picosecond incoherent sum CARS model was developed, validated, and compared to current impulsive and time-independent models with the purpose of improving the picosecond CARS measurements. Further comparisons of the model for vibrational and rotational CARS yield interesting conclusions: for vibrational CARS there is a significant impact on the temperature accuracy when the incoherent sum model is used, while for rotational CARS measurements, the time-independent (nanosecond) model is very similar to the picosecond one in some cases. Furthermore, with the correct pulse parameters, the picosecond incoherent sum model can be extended to be used in the nanosecond and in the femtosecond regime. Computational time comparisons show that the model is 2-3 times slower than the hybrid fs/ps impulsive model.

6. BURST-MODE 100 KHZ N₂ PS-CARS FLAME THERMOMETRY WITH CONCURRENT NONRESONANT BACKGROUND REFERENCING

Modified from a paper published in Optics Letters (2021)

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A burst-mode nitrogen (N_2) picosecond vibrational coherent anti-Stokes Raman scattering (ps-VCARS) system is presented for accurate flame thermometry at 100 kHz repetition rate. A frequency-tripled ps burst-mode laser is used to pump a custom optical parametric generator/amplifier (OPG/OPA) to produce 607 nm broadband Stokes pulses with 120 cm^{-1} bandwidth, along with a narrowband 532 nm pump/probe beam. A simultaneous shot-to-shot nonresonant background (NRB) measurement is implemented to account for Stokes spectral profile and beam overlap fluctuations. The 100-kHz ps-VCARS data are benchmarked in a near-adiabatic CH_4 /air Hencken calibration flame with an accuracy of 1.5% and precision of 4.7% up to peak flame temperatures. The use of N_2 VCARS and simultaneous NRB measurements enables high-speed thermometry for a wide range of fuels and combustion applications. © 2021

6.1 Introduction

High-repetition-rate temperature measurements in reactive environments are essential for the study of highly turbulent combustion systems, detonation wave propagation dynamics in combustors [1], and chemical kinetics in shock tubes [4]. High-speed temperature measurements are also important for model development and validation in high enthalpy transient environments such as hypersonic test facilities [5] and multiphase blasts [63]. Nanosecond (ns) and picosecond (ps) CARS have been widely used for precise and spatiotemporally

resolved measurements of temperature and species concentrations at rates of 10–20 Hz in many combustion applications [12], [17], [103], [134], [135]. In the past 10 years, due to the availability of femtosecond (fs) Ti:Sapphire lasers, hybrid fs/ps [15], [62], [136], [137] and chirped probe fs CARS [138] have enabled temperature measurements at rates of 1–5 kHz [139]. A challenge at higher repetition rates has been to produce a broadband Stokes pulse and a narrowband probe with sufficient energies and precise synchronization. At 10 Hz to 1 kHz, this was achieved by mode-locking fs pulses with a separate narrowband ps laser for line and planar CARS measurements [63], [117], [139]. At 1 kHz, a single fs laser has been implemented with part of the energy spectrally narrowed and amplified, or chirped for frequency or time-domain measurements, respectively [136], [137], [140], [141]. Notwithstanding these efforts, the repetition rate of commercial fs Ti: Sapphire lasers has remained limited to a few kHz. One approach to increasing the measurement rate and track the temperature in highly dynamic flames is to employ a burst-mode laser. Such lasers have enabled many high-repetition-rate measurements, such as particle image velocimetry (PIV), planar laser induced fluorescence (PLIF), Rayleigh scattering, and picosecond laser electronic excitation tagging (PLEET) at rates of at least 100 kHz and as high as 5 MHz in some cases [35], [118]. To increase the repetition rate of CARS with burst-mode lasers, two possibilities have been explored: 1) design of a custom hybrid fs/ps broadband/narrowband burst-mode laser [112] and 2) spectral broadening of high-energy ps pulses from a burst-mode laser [121]. For the first, Smyser et al. built a dual output fs/ps burst-mode laser using Nd:YAG and Nd:glass to demonstrate CARS in an atmospheric temperature N_2 jet at 1 MHz repetition rate [112]. While this showed the possibility of MHz CARS measurements, the extension to flames would still require $\sim 100 \times$ higher laser intensity to overcome the reduced number density at higher temperatures, as well as a broader bandwidth. The second option has the advantage of leveraging the high-energy output of a commercially available ps burst-mode laser, and broadening part of the output to produce a wavelength-tunable broadband stokes pulse using an OPG/OPA. Roy et al. [121] adopted this approach using two beta barium borate (BBO) crystals to generate and amplify a broadband pulse centered at 680 nm, pumped by the second harmonic 532 nm burst-mode output, demonstrating 100 kHz H_2 ps-CARS thermometry in an H_2 jet diffusion flame in air. This showed that high-repetition-rate measurements at moderate flame temperatures are possible, but only in regions where there is significant unburned H_2 . The application to most relevant combustion and flow environments requires N_2 or O_2 CARS thermometry, which necessitates a lower Stokes wavelength (~607 nm and ~580 nm) and 4× or 29× higher laser energy, respectively, due to the smaller molecular Raman cross-section.

The goal of this work is to enable high-repetition-rate CARS thermometry in a wide range of combustion applications using N_2 as the probe molecule. This allows operation with diverse fuels at varying fuel-air ratios and up to peak flame temperatures well over 2000 K. Furthermore, to improve measurement accuracy over prior 100 kHz work [121], an approach to mitigate shot-to-shot ps-CARS signal fluctuations with a silica reference is introduced. The N_2 ps-VCARS measurements are validated and characterized in a CH_4 /air calibration flame and demonstrated in turbulent jet flames.

6.2 OPG/OPA design iterations

The high-speed ps-CARS system employs a single ps-burst-mode Nd:YAG laser outputting $\sim 130 \text{ mJ/pulse}$ with 107 ps pulse duration at 1064 nm. The frequency-tripled 20 mJ/pulse output at 355 nm is used to pump a custom optical parametric generator/amplifier (OPG/OPA) to generate broadband 607 nm Stokes pulses, with the residual frequencydoubled $\sim 10 \text{ mJ/pulse}$ output at 532 nm serving as the narrowband pump/probe for twobeam CARS.

In this section, not present in the optics letter paper, we further describe some of the design considerations and iterations for the stokes pulse generation system.

The OPG/OPA is the result of various design iterations for a setup that could get at least 1-2 mJ/pulse at 100 kHz. Initial testing and iterations were performed using a 10 Hz Ekspla ps laser, which enabled much quicker implementation of the changes compared to the burst-mode laser. A few of the design iteration steps are described here to provide a better idea of the process. The first arrangement was similar to the OPG/OPA setup used by Roy et al. for 100 kHz H_2 CARS[121], involving 2 BBO crystals with an input telescope, as shown in figure 6.1 (a). With this it was easy to get OPG and an amplified

OPA beam out. The energy measured was as high as 4 mJ for the expected input conditions, but the resulting beam quality remained poor: the beam could not be collimated well and the focus was ~ 1 mm even with a short f=100 mm focal length lens. Additionally, the output was ~ $450 cm^{-1}$ resulting in reduced spectral density. An image of the OPG output, which can be seen in the center of figure 6.1 shows that s the phase-matching radial angle increases, the wavelength produces decreases; the OPG crystal could be tuned to change the maximum central wavelength produced, then depending on that and the collimation of the input beam, a certain bandwidth, which may be calculated with the software SNLO, is produced. Because there is a radial distribution in the wavelengths, if the output is not collimated, it will expand in a cone at an angle dependent upon the aforementioned phasematching condition. Figure 6.1 (b) is the application of this concept by simply spacing out the OPA crystal from the OPG. This way the seeding bandwidth is reduced depending on the Δx between the crystals, and the spectral density of the signal beam is improved. The remaining issues are 1) the beam quality is poor and 2) OPG continues to be produced in the OPA stage, even for good temporal overlap. The beam quality issue is mostly due to the fact that the OPG is produced at every location within the BBO crystal, so the output can be thought of as coming from many point sources, throughout the crystal, making it challenging to focus everything into one spot again. Producing OPG in a very small area greatly improves the beam quality. To perform this without damaging the crystal requires to reduce the input energy. Noting that the threshold for OPG for BBO is about $1.2GW/cm^2$, and the damage threshold is $\sim 2.5 GW/cm^2$, only 5-10 % of the input 355 nm could be directed into the OPG section, as shown in 6.1 (c). Successively, various other solutions were implemented, focused on setting the OPG output to the desired characteristics-improved beam quality and select spectral bandwidth.



Figure 6.1. Schematic of sample OPG/OPA iterations. a) Initial setup with 2 crystals; b)Setup with the OPA crystal far enough away to reduce the bandwidth c)Splitting of the OPG and OPA parts to improve the beam quality and conversion efficiency

Additional design tests involved using a spatial filter after the OPG and after the OPA crystal, as well as using between one and three OPA amplification stages with different splitting of the pump beam into these stages. The final design was chosen as a balance between ease of alignment, beam quality and bandwidth. The switch to LBO crystals in the final design was also a key aspect for obtaining the required output. This because BBO was causing a lot of unwanted optical parametric generation, which took away energy from the amplification process, and made it seem like there was plenty of energy available for CARS, when in reality a lot of it was not coherent enough to reach the probe volume correctly and convert to CARS signal. Finally, it should be noted that blocing the idler from the OPG with a shortpass filter reduced the output energy, but avoided the issue we found of two beams being produced. This because the small walk-off caused the idler and signal to be separated slightly at the OPA and produce independent signal/idler pairs. In the future this could be avoided by separating the two and recombining them, as in [[132]], with the risk

of higher setup complexity. Various of the solutions implemented provided excellent results using a stable 10 Hz lase, but did not translate well to the burst-mode, likely due to a $2-3\times$ better beam quality in the Ekspla laser compared to the burst-mode, as well as significant differences in pointing stability, which caused per pulse intensity and/or spectral shift in the OPG output; use of multiple crystals, and less filtering were partially implemented for this reason. The final design is well described in the Experimental section below.

6.3 Experimental Setup

As shown in fig.6.2, 10% of the 6 mm diameter 355 nm beam is down-collimated to ~1.2 mm by a 5:1 telescope to achieve a peak intensity of 1.6 GW/ cm^2 through the 8x8x10 mm long Type I BBO uncoated OPG crystal cut at 32°. A dichroic high-pass 45° mirror (Lattice Electro-optics) is angle tuned to reflect the residual 355 nm and transmit the ~590-615 nm signal and 70% of the idler. The OPG output is collimated by an f = +75 mm planoconvex lens.

After initial experiments, a 700 nm short pass filter (Thorlabs FESH0700) was added to block the idler and avoid amplification of two independent signal-idler beams due to spatial walk off. The initial $\sim 5800 \ cm^{-1}$ bandwidth of the OPG output was reduced to $\sim 300 \ cm^{-1}$ by the spectral filtering described, with an energy of $\sim 15 \ \mu$ J/pulse fig.6.3a. Fig.6.3b. displays the output spectral profile of OPG and OPA. The bandwidth of OPG is further reduced in the OPA because of gain-narrowing. The remaining 18 mJ of the 355 nm burst-mode laser output is down-collimated with a 2.5:1 telescope and time delayed in an antireflection-coated 10 mm long slab of UV fused silica to be temporally overlapped with the OPG seed pulse within the OPA stages. After investigating different crystal types for the amplification stage, lithium triborate (LBO) Type I was selected due to a high enough threshold to avoid a parasitic OPG superfluorescence process common in BBO [132], which removes energy from the amplification process especially if small pulse overlap mismatch occurs during a burst. Although LBO has a lower nonlinearity, it still provided higher energy and beam quality compared to BBO by gain narrowing and avoiding parasitic OPG losses. As shown in Fig.6.3c, use of two crystals is advantageous at lower pump energies. The two 6x6x12 mm long Type I LBO crystals cut at $\phi = 40^{\circ}$ were placed in a walk-off compensating arrangement.



Figure 6.2. Optical layout of CARS system with (a) pump/probe beam and (b) OPG/OPA system. BS: beam splitter; HWP: half wave plate; UVFS: 10 mm AR coated UV fused silica; DM: dichroic mirrors (1) R355 T600–640 nm (> 95%) T850–870 nm (70%) (2) R355 T600–640(>95%), and (3) R600–640 nm T850–870 nm; SPF: shortpass filter; BPF: 605 ± 15 nm bandpass filter.

The first crystal amplifies the pulse from 15 µJ to 0.5 mJ with a small signal gain of ~33, and the second crystal produces ~3.5 mJ of combined signal and idler. The OPG output and the beam in the far field are shown in Fig. 6.3d-e, indicating that some astigmatism is present, probably due to crystal orientation and different M^2 of the pump beam in the horizontal and vertical directions, as described in [118]. The amplified Stokes beam is then separated from the residual pump by a 45° 355 nm mirror, upcollimated, and reflected by a 45° dichroic mirror that allows the idler to pass through. Finally, the beam is passed through a 605±15 nm bandpass filter (BPF) to leave ~2 mJ/pulse at 607 nm for the Stokes beam. The 10% conversion efficiency obtained in burst-mode is lower than the 23% efficiency achieved with a 10 Hz 80 ps laser (Ekspla) used for initial alignment and characterization (Figure. 6.3 a, c), likely due to a longer pulse width and lower 355 nm beam quality. Nonetheless, the burst-mode Stokes energy at 100 kHz and 120 cm^{-1} bandwidth were sufficient for V-CARS at peak flame temperatures. The schematic diagram for the 100-kHz N_2 ps-CARS experimental setup is shown in Fig.6.4 (a). A half wave plate was used to ensure the 532 nm beam was vertically polarized for phase matching in a two-beam CARS arrangement [15]. As shown in Figure 6.3(b), the intensity variation in the 532 nm beam and 607 nm Stokes beams during 1.2 ms burst is <20%. The higher energy of the Stokes pulses in the first 0.25 ms of the burst could result from a smaller 355 nm beam size early in the burst. Fast photodiode measurements (Fig. 6.3c) with a 40 GHz oscilloscope show that the Stokes pulse is reduced to ~75 ps in the nonlinear optical parametric generation process. The measured pump/probe pulse width was ~107 ps. Figure 6.5(a) shows the bandwidth of the nonresonant background (NRB) signal changes over the burst, which increases temperature measurement uncertainty. To account for any bandwidth variations, a single-shot correction scheme was added. Before focusing into the probe volume, 8% of the Stokes and pump/probe beams were reflected by a thin film pellicle beam splitter (Thorlabs, BP208), and the remaining 92% was directed into the measurement volume.

Uncoated 150 mm UVFS planoconvex lenses were used in both legs of the CARS system for focusing and re-collimation of the beams. A 3 mm thick glass window was placed at the probe volume of the 8% reference beam to monitor shot-to-shot NRB signal variation; similar to previous tracking of stokes [142], or NRB in argon [143], with the advantage here of requiring low reference energy due to the higher density of silica compared to argon, and the direct measurement of the nonresonant (as opposed to just measuring the stokes bandwidth). The pump/probe beam was focused to ${\sim}50~\mu{\rm m},$ and the stokes to ${\sim}180~\mu{\rm m},$ producing intensities of 3 and 0.1 TW/ cm^2 , respectively. The length of the probe volume measured by translating a piece of glass was determined to be 1.5 mm at FWHM. Two high-energy 475 ± 25 nm bandpass filters (Semrock) were used to block the colinear pump/probe beams and pass the generated CARS signal beam, while the Stokes beam was diverted into a beam block. Broadband 425–675 nm mirrors were used to direct the CARS signal beam through a 200 mm planoconvex lens and into a 750 mm spectrometer with a 2400 grooves/mm grating. A broadband UVFS prism was used to place the reference NRB signal below the CARS signal. A single EM-CCD camera (Princeton Instruments, Pro-EM-HS 1024) was used to acquire both the dispersed CARS and NRB reference signals at 100 kHz. This was accomplished in the spectra-kinetics mode by focusing the CARS signal at the top 5 pixels and the NRB



Figure 6.3. a) Energy scaling of OPG after filtering and collimation; (b) spectral output characteristics after OPG and OPA with burst-mode pumping; (c) energy characteristics of the OPG/OPA with single and double OPA crystals with 10 Hz 80-ps-duration laser pumping; the red dotted line indicates the energy used with the burst-mode (d) OPG near-field output beam profile; and (e) OPG far-field output beam profile.

reference signal at the bottom 5 pixels of the 1024 1024 exposed region of the camera chip. Two pinholes were placed at the spectrometer slit to limit exposure to the two regions of interest. For each realization of the 100 kHz measurements, the signal on the 1024x1024 exposed region was shifted up by 5 pixels, with the top 5 rows of CARS signal first being binned into a single row before being shifted into a second, masked 1024x1024 pixel array. The bottom 5 pixels with the NRB reference signal are shifted up into the unexposed middle rows of the imaging chip, thereby using the imaging chip to store a sequence of ~200 NRB spectra at 100 kHz, with a spacing of 10 s per burst.



Figure 6.4. (a) Experimental setup with nonresonant shot-to-shot correction, (b) burst profiles for pump/probe and Stokes beams at 100 kHz, and (c) temporal characteristics of the beams, dotted line at FWHM.

6.4 Results

Figure 4b displays a single-shot ps-CARS spectrum of N_2 at an equivalence ratio () of 1. Experimental spectra were processed using a phenomenological vibrational N_2 CARS model described and used previously for hybrid fs/ps CARS [62], modified via an incoherent sum approach to account for the picosecond duration pulses. The shot-to-shot NRB spectra were incorporated into the fitting process to account for bandwidth and beam overlap fluctuations, as described previously [11], [137], [142], [143], and the modeled resolution was adjusted to reduce spectral noise influence. Validation measurements were performed in a methane/air

Hencken calibration burner with a $25 \times 50 \ mm^2$ outlet. The probe height was set to 10 mm above the top of the burner to ensure equilibrium temperatures for equivalence ratios from 0.7 to 1.3. Data were collected from 10 bursts (\sim 700 data points) for each equivalence ratio. An average accuracy of 1.5% and precision of 4.7% was achieved from 1800 to 2225 K, as shown in Fig. 6.5c,d. The latter represents an improvement of $\sim 2x$ through the use of the NRB reference beam but may be limited by high-frequency quantum noise features from optical parametric generation, as detailed in [144]. Note that the low temperature sensitivity of the vibrational CARS spectra was improved by tuning the Stokes beam so that the nonresonant peaked at $\sim 2275 \ cm^{-1}$ between the v = 2 and v = 3 bands, similar to an approach used by [145] for rotational CARS. This enhanced sensitivity to weak hot bands at lower temperatures down to \sim 700 K, reduced saturation of the stronger v = 1 band to allow higher camera gain, and also covered the v = 3 and v = 4 bands well beyond 2000 K. Below ${\sim}700$ K, spectral fitting could still be performed, but the near absence of any vibrational bands except v = 1 leads to higher uncertainties. Accurate measurements below 700 K may be feasible, however, with further optimization of the Stokes beam wavelength to reduce saturation of the v = 1 band as camera signal is increased. After validation of the measurement technique in a well-characterized laminar flame, 100 kHz measurements were demonstrated in an H_2/N_2 turbulent jet diffusion flame issuing from an 8 mm nozzle into static air, as well as a $CH_4/H_2/N_2$ DLR A turbulent jet diffusion flame [31] issuing from the same 8 mm nozzle into a 30 cm diameter air co-flow with a flow speed \sim 30 cm/s.

The reactants were regulated by mass flow controllers (Omega) with a $\pm 2\%$ flow accuracy. The turbulent H_2/N_2 jet with a flow of 16 slpm of H_2 and 4 slpm of N_2 corresponded to a Reynolds number of ~5000 and theoretical adiabatic temperature of 2334 K. The DLR A flame at a flow of 28.1 slpm of CH_4 , 42.23 slpm of H_2 , and 56.85 slpm of N_2 , corresponded to a Reynolds number of 15,200 with theoretical adiabatic temperature of 2,130 K. Both flames exhibited lower temperatures in the inner core 32 mm above the flame where unburned reactants mixed with combustion products. A burst length of 1.1 ms was recorded for the $H_2/\text{air } N_2$ flame and 0.8 ms in duration for the DLR A flame, as shown in Fig.6.6, providing effective measurement durations of ~0.7 and ~0.4 ms respectively, due to flashlamp ramp-up time. In contrast to the relatively steady Hencken burner flame and the lower



Figure 6.5. a) Single-shot NRB reference spectra at beginning and end of burst, with average over the burst; indicates standard deviation of the NRB spectral shift at FWHM; (b) sample single-shot fit from Hencken burner at = 1 with signal-to-noise ratios of 20–100; (c) histograms for two conditions; vertical dotted and continuous lines indicate the theoretical and average measured flame temperatures, respectively; (d) theoretical and experimental temperatures at varying .

Reynolds number H_2/N_2 jet diffusion flame, the data from two separate bursts of the DLR A flame (labeled flame 1 and 2) show more substantial temperature variations of ~1000 K, in some instances with minimum temperatures that dip below the sensitivity range of the vibrational ps-CARS measurements. Note that the DLR A flame is specially formulated to allow benchmark Rayleigh scattering thermometry because of minimal variations in Rayleigh scattering cross-sections in the fuel, air, and products. In comparison to a previous work by the co-authors using 100 kHz Rayleigh scattering [31], the variation in the time scales and temperatures for the DLR A flame in the current work are in good agreement for the same flame condition and location. Also in good agreement are temperatures measured at $\sim 1,000$ K below adiabatic within the core of the diffusion flame.



Figure 6.6. Sample burst-mode ps-VCARS temperature measurements in a Hencken burner, in an H_2/N_2 turbulent jet diffusion flame, and from two separate bursts in a DLR A turbulent jet diffusion flame (labeled flame 1 and 2). Error bars indicate ± 1 .

6.5 Conclusion

In summary, a 100-kHz N_2 ps-VCARS system for accurate high-speed thermometry in turbulent reacting flows was developed and demonstrated. This was accomplished via a custom-built ps burst-mode OPG/OPA pumped at 355 nm, along with an efficient scheme for simultaneous NRB referencing. The system achieved an accuracy of 1.5% and precision of 4.7% in a steady adiabatic flame and was applied to two turbulent combustion environments, with the use of nitrogen being useful in a wide array of fuels and dynamic flames in practical combustion devices. Higher repetition rates may be achieved with increased pump energy and beam quality, with in-situ referencing to improve accuracy [146]. The system can also be extended to CARS measurements of O_2 or other species.

7. 100 KHZ BURST-MODE PICOSECOND VIBRATIONAL N₂ CARS THERMOMETRY IN ENERGETIC COMBUSTION ENVIRONMENTS

Modified from a conference paper published in 2022 AIAA Scitech conference proceedings Daniel K. Lauriola, Alex D. Brown, Paul S. Hsu, Naibo Jiang, Sukesh Roy, Terrence R. Meyer, and Steven S. Son

High-repetition-rate spatially and temporally resolved temperature measurements are needed for modeling and understanding the dynamics of high enthalpy and high-speed combusting environments, such as in shock tunnels, rotating detonation engines, and explosive fireballs. Here we show the application of a recently developed burst-mode picosecond Coherent Anti-Stokes Raman Scattering (ps-CARS) system for vibrational nitrogen gas temperature measurements with high spatiotemporal resolution at 100 kHz rate, with concurrent nonresonant background referencing. This system was applied to study the dynamics of nitrocellulose fireballs and electronic ignition matches to form an understanding of the temperature evolution of the gas phase within the fireball and provide a comparison to the particle phase temperatures obtained by blackbody emission pyrometry. Measurements show there is a significant temperature difference between the hot burning energetic particles and the gas phase, which is being heated in time by the burning particles. The measurements of the e-match plasma indicate the presence of a very hot, non-equilibrium environment during ignition.

7.1 Introduction

Fireballs and multiphase blast detonative events are of interest for agent defeat[147], defense, and weapon development[148]. Accurate modeling of the dynamics of energetic events is essential to the development of more reliable and effective explosives. Direct experimental comparison to models has been the most effective method for validating simulated

results and rapidly improving predictions and designs. The important parameters to consider when validating a model are spatiotemporal dynamics of the solid and gas phases, chemical composition and equivalence ratios of the energetic materials, and temperature of the expanding event. Various experimental techniques have been developed and used to validate and improve current detonation modeling since the 90s. Averaged and pressure measurements depending upon particle traps, lollipop probes and spinning barrel targets have all contributed in some way to obtain statistical data [149] [4-5]. For improved spatial resolution particle image Velocimetry (PIV) was first used by Jenkins et al.[37] to obtain single shot snapshots of the particle field in the fireball. Schlieren, in 2D and 3D has also been valuable for probing the shock expansion dynamics; some recent experiments at 100s of kHz can provide mm resolution of the shockwave [38]. At a smaller scale, digital inline holography with phase conjugate mirrors to overcome phase distortions induced by the change in refractive index over the wave, made it possible to probe small scale shock events at 1 MHz repetition rate, with extremely high spatial accuracy [33]. All these efforts have enabled qualitative measurements of the particle [2], [3], gas phase [33], and shock fronts [36] in fireballs and in detonators. Beyond imaging, work has also been successfully performed to capture the evolution of certain chemical species in detonative environments: iodine laser induced fluorescence enabled tracking of biocidal expansion and propagation in agent defeat fireballs [150], MHz OH planar laser induced fluorescence (PLIF) was used to track shock wave evolution in a rotating detonation engine [115], and wavelength modulated absorption has allowed to simultaneously measure temperature, H_2O and iodine in HMX fireballs at >100 kHz [151]. Temporally and spatially resolved temperature characterization of a detonative event remains a challenge. Two lasers with different excitation wavelengths and two camera imaging systems are typically required for two-color OH PLIF thermometry [152], although recent efforts have simplified the setup to a single OPO and camera [153], the measurements have been limited to 20 kHz and reduced temperature range [43]. Raman scattering has been used at 3 kHz in a shock tube [5], but proves to be a challenge due to the high pulse energy (0.5 J/pulse) required. Absorption spectroscopy has been used at MHz rates with high temperature accuracy, yet remains spatially averaged [151]. On the other hand, coherent anti-stokes Raman scattering (CARS) has proven itself as promising for this application. Single shot measurements have been successfully performed in nano-thermites [154] and RP-80 detonators using hybrid fs/ps CARS [63]. At higher repetition rates, 100 kHz H₂ CARS thermometry was performed in a jet flame [22], as well as demonstration 1 MHz N₂ CARS thermometry in a room temperature N₂ flow [112]. In this paper we demonstrate the use of a recently developed burst-mode CARS system for 100 kHz nitrogen flame thermometry measurements [19]. We show the characterization of the system in an adiabatic flame, and the application to nitrocellulose fireballs. The measurement is simultaneous with imaging and emission pyrometry enabling the determination of the probe volume location and comparison of the particle phase (pyrometry) temperature to the gaseous phase (CARS).

7.2 Experimental setup for CARS and pyrometry

The CARS experiments were performed using a newly developed burst-mode pumped solid state nitrogen picosecond CARS system. The CARS system shown in Figure 1 was pumped by the second and third harmonics of a burst-mode picosecond laser at 100 kHz. The pump energies were 20 mJ for 355 nm and ~8 mJ for the 532 nm beam, with a ~ 110 ps pulse width. The 532 nm pump/probe beam is sent through the system and appropriately delayed to match the Stokes beam in time and space. The 355 nm beam is used to generate, through optical parametric generation (OPG) and amplification, a broadband, 120 cm⁻¹ full width half max, 75 picosecond beam centered at 607 nm, set for a Raman Shift of 2330 cm⁻¹, corresponding to the vibrational band head of the =1 level of N₂. Ten percent of the beam is diverted by a beam splitter (lattice optics), reduced from 6 to ~1.2 mm and passed through an uncoated 8x8x10 mm type II beta barium borate (BBO) crystal cut at 32.5°.

The broadband output produced by optical parametric generation (OPG) was maximized to 607 nm, and bandwidth narrowed by a high transmission 600-640 nm mirror, reflecting 355-600 nm, then collimated by a 75 mm planoconvex lens. A short pass 700 nm filter was added to block the idler, as the signal-idler walk-off produced two signal and two idler beams after optical parametric amplification (OPA). The OPG is pumped at 355 nm with 2 mJ, and outputs a 15 μ J, 300 cm⁻¹ beam centered at 607 nm. The remaining 18 mJ of 355 nm light pass through a half wave plate, are delayed by a 10 mm antireflection coated



Figure 7.1. Optical layout of CARS system with pump/probe (light green) on top, and OPG/OPA. BS: beam splitter; HWP: half wave plate; UVFS: 8 mm AR coated UV fused silica; BBO: beta barium borate type 2 crystal; DM1: dichroic mirror high-pass >95% transmission 600-640 nm, reflect 355-600 nm; SPF: shortpass filter; DM2: reflect 355 nm transmit AR coat 590-640 nm; LBO: lithium triborate type 2 crystal; DM3: high-pass reflect 600-640 nm; BPF: 605 ± 15 nm bandpass filter

UV-fused silica window, and down collimated to 2.4 mm by a 2.5:1 telescope. The pump is then recombined with the OPG output via a 355 nm high energy mirror, AR coated on the back side for 600-640 nm transmission. The 607 nm seed beam is amplified by two optical parametric amplification (OPA) stages, consisting of two walk-off compensated 6x6x10 mm lithium triborate (LBO) crystals. The two amplification stages produce a 2.5 mJ gain narrowed beam with signal and idler, after removal of residual 355 nm by a high reflection 355 nm mirror. The ~2 mm beam is expanded to 8 mm, and the idler is transmitted through a dichroic mirror (DM3) reflecting 600-640 nm, transmitting 800-840 nm. Energy measurements of the expanded stokes beam are performed after a 605 ± 15 nm (Semrock) bandpass filter to eliminate any residual 355 and idler. Measured energy of the final stokes beam was 1.25 mJ/pulse. The CARS system was integrated into the experimental setup shown in Figure 2. The two-beam output of the CARS system was split by an 8/92 thin film pellicle beam-splitter. The high intensity part was sent into the probe volume, and the CARS signal directed into a 0.75 m spectrometer and dispersed onto a high speed EMCCD camera (ProEm HS – Princeton Instruments). The remaining 8% of the beam was directed into a 3 mm piece of UVFS glass to obtain CARS reference non-resonant background spectra. The nonresonant signal was focused into the spectrometer right below the CARS signal so that it hit the bottom of the camera chip and could be used for shot-to-shot referencing.



Figure 7.2. a) Experimental setup for flame calibrations, and fireballs experiments, with non- resonant background single shot correction. A high-speed camera (Photron SaZ FastCam) was used for emission imaging to track burning particles through the probe volume, while a pyrometry color camera with a three-band filter measured blackbody emission; b) View of the ps-CARS system, pumped by the burst-mode laser (not shown); c) top and side view of the chamber for the fireball experiments before and during a test.

A high speed Photron SAZ camera was used to perform 100 kHz imaging of the probe volume, to monitor the location of the fireball throughout the CARS measurement burst. On the opposite side a color pyrometry camera was placed to determine 2D gray body temperature of condensed phase combustion products at 1 kHz, utilizing a custom triple bandpass filter in combination with the red-green-blue (RGB) Bayer filters on the camera. The ratio of signals between the color channels provides a temperature based upon a Wien approximation of the Planck black body distribution, the details of which are outlined elsewhere [155]. Initial system calibrations were performed with a Hencken burner in the probe volume, to characterize the temperature precision and accuracy of the CARS system at 100 kHz repetition rate and ensure that the data analysis code used performed as expected for data fitting. For the fireball experiments a 6"x6"x 6" blast chamber, previously described in [150], and shown in fig. 2c was used. The experiments were performed by adding Nitrocellulose and black powder mixtures into a 3D printed container with a conical geometry to create a deflagrating fireball, as shown in the center of fig.2c. Nitrocellulose was chosen to simulate a propellant fireball and create an optically dense fireball $(OD \sim 0.8-1)$ as a metric to test the feasibility of the CARS setup in a high explosive environment. The mixture was initiated using a commercial electric match device. The electric match consists of a wire coated with a pyrotechnic mixture. A 4kV electrical pulse is discharged across the electric match using a Teledyne Risi FS-43 triggering unit, igniting the pyrotechnic and kickstarting the deflagration of the nitrocellulose and black powder. The Teledyne Risi FS-43 also outputs a TTL signal that was used to trigger the burst-mode laser and camera equipment. In this way, it was possible to delay the 1 ms laser burst to probe different times during the fireball evolution. Later, experiments were also performed solely with the electric match to obtain the temperature of the ignition plasma.

7.3 Results

Measurements in a flat-flame Hencken burner were initially performed with and without nonresonant shot-to-shot referencing. While the results without a reference showed $\sim 8\%$ uncertainty, the use of single shot referencing, as described in the experimental setup, enables

to correct for variations of bandwidth and overlap of the beams, resulting in a 1% precision and a 4.8% accuracy on average over the calibrations performed in the CH4/air Hencken burner from Φ =0.7 to 1.3. Figure 3 shows sample fitted Hencken burner spectra, for a nonresonant pumping centered around 2285 cm⁻¹, and sample histograms of 10 bursts for two equivalence ratios. For later experiments in the fireballs, the stokes bandwidth peak was shifted to ~2310 cm⁻¹ during signal optimization, and these results were used to determine the expected experimental uncertainties for the following experiments in fireballs.



Figure 7.3. Hencken calibration results: a) Sample spectrum and temperature fit for $\phi = 1.0$ b) Histograms over 10 bursts for two equivalence ratios.

Sample imaging and thermometry results in a nitrocellulose fireball are shown in Figure 4a-b. The visible emission imaging is used to provide an indication of the fireball evolution during the measurement period. The CARS measurement, delayed 8 ms from initiation, is temporally aligned to the visible emission to better understand the dynamics. The pyrometry camera provides a single snapshot of the temperature from blackbody emission before, during, or right after the CARS measurements. The high speed camera enabled monitoring of the probe volume to check whether the CARS beams collided with and ignited unburnt particles, and whether many burning particles were present near the probe volume. In the case of these events, the data points in which the laser hit and burned particles were discarded as the purpose of the CARS was to measure the N_2 gaseous phase, complementary to the information provided by the pyrometry which measured blackbody particle emission.



Figure 7.4. a) Visible emission images of the nitrocellulose fireball at the beginning of the burst and after 270 µs; b) temporal dynamic at the probe volume highlighted in green in a, as measured by CARS; c) Pyrometry image right after the burst d) 2D temperature obtained from pyrometry measurements

The pyrometry measurement (Figure 4c-d) shows the emitted temperature over the entire burst. The blackbody temperature was obtained throughout the entire 45 mm diameter viewport, except for the areas close to the CARS probe volume. In the highlighted white region in Figure 4d the scattering of the 532 nm beam caused saturation in the pyrometry camera, making it impossible to obtain a temperature measurement at the exact probe location. Saturation from a 532 nm beam reflection is also noticeable in the top part of the figure. This can be overcome in future experiments by simply adding a 532 nm notch filter in front of the pyrometry camera measurements within the probed CARS region also. Measured pyrometry temperatures are in the range of 2,000 K to 2,800 K, as shown in figure 4d, much higher than the 1,500 K peak temperature from CARS in this run. This is understood due to the nature of the measurement: pyrometry collects the average blackbody thermal radiation from the fireball and is biased towards higher temperature emitters, likely from the outer region of the fireball, while low temperature N_2 areas have less influence on the measurement. The minimum temperature that can be measured by pyrometry is $\sim 1,500$ K. Ten tests were performed in Nitrocellulose fireballs to determine what trends the temperature in the fireball followed, as well as whether the gas temperature was repeatable. Use of the pyrometry, and especially the 100 kHz visible imaging, nicely complemented the CARS measurement by providing information on how close burning particles were (high speed camera) and the temperature of the blackbody particles (pyrometry), although this was obtained as the average over the entire burst and with the aforementioned limitations due to the camera's 1 kHz repetition rate. Figure 5 a shows three sample measurements and figure 5b shows the temperature results for the shown fireball still-frame. The composition of the fireball was kept the same, but the delay and consequently the probe location with respect to the fireball were varies. In the first we observed a large amount of burning/luminous particles in proximity of the CARS measurement volume. The second test was taken once the leading edge of the fireball had passed, and happened to be in an area with fewer burning particles. The third test was at an early delay, which meant that the fireball front only started passing through the measurement volume at $\sim 300 \ \mu s$ from the start of the burst. It should be noted that that the test 3 results only extend to 620 µs due to ignition of some particles by the laser in the later pulses of the burst; most of the test3 measurements in the beginning of the burst are all at ~ 300 K as there is no fireball in the probe volume; at such low temperatures (300-700 K), the uncertainty of vibrational CARS fitting may be higher due to the lack of a secondary band ($\nu = 2 \rightarrow 1$ level).

The results from the fireball experiments seem to indicate that in the experiment the air is not heating up uniformly during the event, and how much a certain area heats up depends on the burning particle concentration; this is particularly pronounced in this kind of energetic deflagrative environment where there is no shock-wave inducing a sudden temperature change in the gases it passes through. Further experiments were performed with only the primary igniter to determine the initiation temperature of the fireballs. For this part the incoherent sum picosecond CARS analysis code, described elsewhere [19], was modified to accommodate



Figure 7.5. Sample fireball images for three nitrocellulose cases; b) temperature measurements from three nitrocellulose fireball tests, chosen for the presence or absence of burning particles near the probe volume.

for nonequilibrium temperature fitting, by allowing the least squares optimization procedure to find minima for both rotational and vibrational temperatures, as a hot plasma could be expected to be in a highly non-equilibrium state. Although an additional neutral density filter was added onto the high-speed imaging camera for the e-match experiments, some intensity saturation was still present. A visible image of the e-match at 80 µs and sample spectra over a span of 80 µs are shown in figure 6a and 6b respectively. Pyrometry measurements of the e-match were also taken (Figure 7c), although these were made more difficult by the absence of large burning particles, and the fact that plasmas can distort blackbody emission to appear at a lower temperature, as has been described in literature [156]. Sample temperature fits of the plasma are shown in figure 7a, and the full temperature profile over a burst is shown in figure 7b. Figure 7c shows the result of the temperature calculated from the pyrometry. From the CARS measuremeents we noted a large difference between the rotational and vibrational temperatures in the very beginning of the event.



Figure 7.6. Experimental measurements of an electronic match: a) Visible emission image at $t = 80 \mu s$, and b) Sample single shot spectra of the plasma induced by the e-match.

The temperature fits indicate that this the rotational temperature is ~400-800 K, while the vibrational temperature is close to 4,000 K. Later in the burst, after the most intense part of the plasma has passed, the vibrational temperature falls, almost meeting the rotational temperature ~1,000-1,500 K. It should be noted that calibrations were performed for equilibrium conditions, so the exact uncertainty of the ro-vibrational results is undetermined. A high uncertainty could make it challenging to determine whether or not the gas is in equilibrium in the last 300 µs of the shown burst as shown in figure 7, but the non-equilibrium in the first 400 µs remains obvious. More accurate determination of the ro-vibrational relaxation could be obtained by increasing the spectral resolution to resolve rotational lines, as well as by monitoring both the P and the Q branches of N₂ as has been previously done by Dedic et al.[157].

The pyrometry results (figure 7c) seem to indicate a blackbody temperature up to 2,600 K, yet in various areas (in white) of the measurement the signal was too low, to perform the



Figure 7.7. a) Sample nonequilibrium fits of rotational and vibrational temperature to the CARS spectra in the e-match b) Result of measured vibrational and rotational temperatures for the e-match test; c) pyrometry temperature averaged over the entire burst (~ 2 ms).

blackbody fitting, or saturated by the laser. Additionally, the distortion of the blackbody spectra in the presence of a plasma has not been studied by us thoroughly, and it is our expectation that some separate calibrations in a plasma, compared to a blackbody, would be necessary to obtain valuable results.

7.4 Conclusion

In this chapter we presented a burst-mode pumped system for measuring N₂ temperature with a 0.5 mm spatial resolution at 100 kHz repetition rate in optically dense (\sim OD=1) nitrocellulose fireballs. The measurements were complemented by 100 kHz visible imaging and 1 kHz blackbody emission thermometry to provide more information at the measurement volume. The 100 kHz time scale allowed to track the gas temperature dynamics, related to the vicinity of burning particles in nitrocellulose fireballs. The pyrometry was a proof-ofconcept measurement that, with improved repetition rate, filtering and calibrations, could nicely complement the CARS measurements by providing the particle, rather than the gas temperature. Measurements in a plasma produced by an e-match were also performed to find that non-equilibrium temperatures can be measured with this system, and the excellent time-resolution may help determine the evolution of the non-equilibrium plasma; and could be further improved by monitoring the N_2 S-branch at the same time as the Q-branch with CARS by using the same arrangement, by directing the overlapped probe and rotational CARS beams into a different spectrometer, after filtering out most of the probe intensity. Additional measurements of energetic thermites, and detonators which have event durations on the order of a few milliseconds, and 100s of microseconds respectively, for which temperature has been characterized on a single shot basis only, are of high interest for this technique. The better understanding of the temperature dynamics provided by the time-resolved CARS measurements may also be coupled to the well-developed Particle Image Velocimetry and Schlieren techniques to quantify the gas-particle-expansion wave interplay in high energy explosives. The technique may also be applied to measure shock wave propagation in other environments, such as in a rotating detonation engine.

8. 100 KHZ PS-CARS APPLIED TO A HIGH ENTHALPY FREE-PISTON SHOCK-TUBE AT SANDIA NATIONAL LABORATORIES

Modified and expanded from a paper published in 2022 AIAA Scitech conference proceedings, by Sean P. Kearney, Kyle A. Daniel, Justin Wagner, Kyle P. Lynch, and Charley R. Downing, Daniel K. Lauriola, Jason Leicht and Mikhail N. Slipchenko

Coherent anti-Stokes Raman scattering of the N_2 molecule is performed at rates up to 100 kHz for thermometry in the Sandia free-piston, high-temperature shock-tube facility (HST) for reflected-shock conditions in excess of T = 4000 K at pressures up to P = 10 atm. A pulse- burst laser architecture delivers picosecond-duration pulses to provide both the CARS pump and probe photons, and to pump a solid-state optical parametric generator (OPG)/optical parametric amplifier (OPA) source, which provides frequency tunable Stokes pulses with a bandwidth of 100-120 cm⁻¹. Single-laser-shot and averaged CARS spectra obtained in both the incident (P = 1.1 atm, T = 2090 K) and reflected (P ~8-10.5 atm, T > 4000 K) shock regions of HST are presented. The results indicate that burst-mode CARS is capable of resolving impulsive, high-temperature events in HST.

8.1 Introduction

Temporally dynamic applications in hypersonic systems and energetic materials are receiving renewed interest. These applications are characterized by fast time scales in the associated physical processes and, in many cases, short (μs to ms) test durations. These highly transient environments additionally present significant measurement challenges characterized not only by fast time scales, but extreme conditions in temperature, pressure, heat-flux, and luminosity— which in many cases can only be probed by noninvasive measurement tools, such as laser diagnostics. Coherent anti-Stokes Raman scattering (CARS) is a powerful and well-established method for noninvasive gas- phase thermometry and species detection [12]. The method enables measurements across a wide range of conditions and in challenging environments, from low-temperature compressible flows [158]; combustion [96], [159], [160], and, most recently, in high-enthalpy testing for hypersonic applications . CARS requires three input laser photons, two for pump/Stokes preparation of a Raman coherence and a third to probe the induced Raman polarization. For single shot broadband CARS detection, one or both of the pump/Stokes sources must operate with enough bandwidth to enable detection of the full Raman spectrum on a single-laser-shot basis. For gas-phase diagnostics, this has most often been achieved using nanosecond-duration Nd:YAG and dye-laser systems with repetition rates near 10 Hz, and broadband dye laser bandwidths of 100-300 cm^{-1} or more [17], [96], [99], [159], [160]. More recently, amplified femtosecond laser systems have been utilized for CARS pump/Stokes preparation, with repetition rates as high as 5 kHz [138], [161]. This impressive data rate nevertheless is inadequate for time resolution of hypersonic and energetically driven events, reducing most modern laser diagnostics to single-shot devices for these applications.

On the other hand burst-mode Nd:YAG lasers have helped researchers overcome the speed barrier associated with repetitively pulsed laser systems with a low-duty-cycle operating condition that permits overdriving the lasing medium at 100s of kHz to MHz rates in short, ms-duration bursts [41], [111]. These systems were first demonstrated as fixed- wavelength sources for high-speed flow visualization, and have since seen significant development for quantitative, chemically-specific diagnostics when coupled with tunable optical parametric oscillators. To date, tunable pulse-burst OPO systems have been most often applied for laser-induced fluorescence detection [44], [45], [114], where the frequency narrow operation of colinear phase-matched and injection-seeded OPOs is well-utilized for diagnostics. Operation of a spectrally broadband source at high repetition rates represents a key technical barrier for application of burst-mode CARS, which has recently been overcome by Roy et al. [121], who demonstrated single-shot acquisition of H_2 CARS spectra at 100-kHz rate by utilizing high-intensity picosecond laser pulses for broadband optical parametric generation (OPG) and subsequent optical parametric amplification (OPA). Lauriola et al.[19], have improved upon this OPG/OPA idea to obtain higher intensity output and demonstrate 100-kHz N_2 CARS thermometry in laboratory flames. Smyser et al. [112] have also very recently demonstrated a new combined femtosecond/picosecond burst-mode laser system for "hybrid" pure-rotational CARS measurements in room-temperature N_2 . This system has great potential because the transform-limited performance of femtosecond laser pulses delivers superior broadband low-noise pump/Stokes preparation relative to picosecond or nanosecond broadband sources, which necessarily exhibit poor coherence; however, the 270-fs, $\sim 50 cm^{-1}$ pulses delivered by this burst-mode system do not yet provide sufficient bandwidth or energy for high-temperature applications.

In this study, we apply the picosecond OPG/OPA-based scheme for 100-kHz CARS to the challenging environment presented by Sandia's free-piston-driven, high-temperature shock-tube (HST) facility. HST presents a significant challenge for virtually any laser-diagnostic instrument. The facility can achieve extreme temperatures, in excess of 10,000 K, at pressure of 10s to 100s of atm, with high levels of mechanical vibration and luminosity. In this work, we demonstrate single-laser-shot acquisition N_2 CARS spectra at 100-kHz rates at temperatures in excess of T = 4000 K and pressures to P = 10 atm, using pure N_2 as the test gas. This work is a follow-on to our recent demonstration of spontaneous Raman thermometry in HST using a similar burst-mode laser [5]. Transition from spontaneous Raman to CARS provides for higher signal levels, which enable us to access to higher temperature, lower pressure test regimes. The coherent, laser-like nature of the CARS signal beam additionally provides for effective rejection of background luminosity.

8.2 Experiments

The Sandia free-piston high-temperature shock tube (HST) facility is described in detail elsewhere [162] and is briefly summarized here. A schematic of the shock tube setup is shown in figure 8.1 A reservoir section is filled with N_2 at pressures of 7–28 atm, is used to launch the 11.9-kg piston down the shock tube's driver section. The driver-gas section has a length of 5.2 m and an inner diameter of 0.267 m, and is separated from the driven test-gas section test gas by a steel diaphragm. The driven section is composed of four modular tubes, with a total length of 9.2 m, and an inner diameter of 0.087 m. The test section is located at the end of the driven section to allow maximum separation between the incident shock wave and the contact surface interface between the test gas and the downstream- propagating driver section gas—thereby maximizing the useful test time. In each experiment, the piston is propelled at several hundred m/s to isentropically compress the driver gas to very high temperature and pressure. Upon shock reflection from the test-section end wall, a substantial fraction of the work input from the piston is recovered in the test gas to reach temperatures in excess of 4,000 K. A key goal of this study was first to obtain relevant CARS measurements at ~2,000-3,000K and then assessment our ability to measure temperatures in the T = ~4000-5000 K range using 100 kHz pulse-burst N_2 CARS.



Figure 8.1. Schematic setup of the shock tube and laser arrangement a) schematic of the shock tube and lasers b) top view of the probe section where the actual CARS measurements were performed

Each shock-tube experiment is characterized by three thermodynamic state conditions in the test gas: State 1 is an unshocked pre-test state at room temperature and low pressure;
State 2 is the condition after passage of the incident shock wave through the test section; and State 5 is the highest temperature and pressure condition reached upon the passage of the shock reflected from the test-section end wall. These states are modeled with a simple back propagating iterative solver before and after the event. Before the event the gas compressibility ratios and initial conditions are used to obtain the expected values, while after the experiment the pressure transducer values can be used to obtain more accurate state-average solution estimates. Figure 8.1 showed some pressure transducers which enabled tracking of when the shock arrived and were used to perform trriggering of the laser. The traces from these and from a photodiode measuring the stokes beam are shown in figure 8.2. This could have also been used to determine at which point in the spectral acquisition the shocks passed by, but we will later see that it was quite obvious.



Figure 8.2. Photodiode and pressure traces of the lower enthalpy test

CARS spectra have been acquired at 100-kHz rates using a picosecond burst-mode laser and OPG/OPA arrangement thoroughly described in previous sections. The burst-mode laser system (Spectral Energies, QuasiModo) is similar to that described in [163]. A 1064 nm cw diode source, is chopped to a 100-kHz train of ~80 ps pulses by a fiber-based electrooptic modulator (EOM). After initial fiber amplification, these seed pulses are then gated using a fiber-coupled acousto-optic modulator (AOM) to eliminate remaining cw background and amplified in multiple stages of flashlamp-pumped Nd:YAG amplifiers. The 1064-nm fundamental is frequency doubled and tripled, resulting in nominal pulse energies of 13 mJ

and 21 mJ in the 532 nm and 355 nm outputs, respectively. The 532 nm second-harmonic beam is ~ 60 ps FWHM in duration and serves as a single, combined pump and probe in a twobeam CARS configuration, with pulse energies from 5-10 mJ incident upon the shock tube test-section windows. The Stokes source is generated using a similar OPG/OPA arrangement to the one described by Roy et al. [121]. ~6of the 355-nm second harmonic pulse is split from the main beam and down-collimated by $5 \times to$ provide a high-intensity source for optical parametric generation in an 8-mm-long BBO crystal. The resulting spectral bandwidth was over $200 cm^{-1}$, centered near 606 nm, and was amplified by the remainder of the 21-mJ pump pulse in two 6 mm long LBO crystals arranged in a walk-off compensating geometry. The resulting ${\sim}1.5{-}2.5~{\rm mJ}$ Stokes pulses were ${\sim}55{-}60~{\rm ps}$ in duration and 90 to 120 cm^{-1} FWHM bandwidth. The Stokes pulse was up-collimated by $5 \times using a Galilean telescope, whose$ element spacing was adjusted to match the focal locations of the pump and Stokes beams at the CARS measurement volume. The two beam CARS arrangement was propagated by a series of dichroic mirrors to a f = 125 mm singlet beam-crossing lens as shown in figure 8.1b. This short focal length was necessitated by the 76-mm inner dimension of the HST test section. The signal might have benefited from longer beam-crossing lenses, but resulted in small beam sizes at the 25.4-mm-thick sapphire test section windows and resulted in window damage, and initially caused issues with nonresonant signal generation in glass. The 473-nm CARS signal beam emerged collinear with the residual 532-nm pump/probe radiation. A series of dichroic mirrors passed the intense pump radiation, while reflecting the majority of the CARS signal to the entrance slit of a 0.75 m spectrograph, equipped with a 1800 1/mm grating. Alignment of the CARS beam through the spectrometer was facilitated by using the residual 532-nm light from a cw alignment diode laser that propagated with the CARS pump beam; a key advantage of the two-beam arrangement for burst-mode operation in a test-facility environment. The CARS spectrum was detected with a dispersion of \sim $0.33 cm^{-1}$ /pixel using a backside-illuminated, electron-multiplying CCD camera (Princeton Instruments PRO-EM). This CCD camera is capable of providing high spectral acquisition rates by shifting charge vertically upwards from a light-exposed region of interest in a userdetermined vertical bin height. In this manner, the majority of the both the 10242 pixel light-sensitive portion of the chip and an additional masked 10242- pixel region can be used to store charge that has been accumulated through the duration ~150 pulse burst, and the resulting CARS spectra are then digitized at the end of the dynamic shock-tube experiment. This high-speed detector architecture requires that minimal background light falls on regions of the chip other than the 5 to 10 pixel-high region of interest where the CARS signal falls, which can represent a significant challenge in high-temperature shocktube experiments with high levels of background emission. This background emission was mitigated using, a spatial filter with a $200\mu m$ diameter aperture at its focus in the CARS collection optics. An additional $100\mu m$ diameter pinhole was placed near the slit plane of the spectrograph during the later particularly high-temperature shots for additional background rejection.

8.3 Results and Discussion

As nonresonant background referencing wasn't used for this application due to the short setup timeline and already significant complexity, and the fact that the shock tube could be run at best ~2-3 times per day, the expected uncertainty of the measurements was around 10. Nonetheless Hencken calibrations were performed in an H_2/air Hencken burner from average burst data, as shown in figure 8.3 to confirm experimental accuracy over a range from ~1,000K to ~2,500 K. Although the fitting was consistent, the resolution of the spectra was found to be much lower than in previous experiments, with a fitting resolution of $4.4cm^{-1}$ as shown in figure 8.3



Figure 8.3. Three sample spectral fits of the Hencken burner calibrations

Results from an initial lower temperature ($\sim 3,000$ K) event are shown here, as well as the state dependent comparison to the model. First we see a 2D map of the spectra over the whole event. The transitions between states are quite obvious and don't even need to be highlighted.



Figure 8.4. 2D map of the spectra for one of the initial experiments

The spectra obtained is fit and then compared to the state average temperature determined by the pressure transducers. From figure 8.5 we observe that at room temperature, before the shock, there is a large amount of variation in the fitting. This is because vibrational CARS only shows one main peak (v=0) up to 1,000 K, so the uncertainty is expected to be high, as much as $\sim 50\%$ in some cases. The incident and reflected shocks fall within, or slightly above the calibration range of the measurement technique, so we see very good agreement between the two. Finally, when the argon contact surface reaches the probe volume, CARS shows a much lower temperature. Here, the spectra shows a significant increase in the nonresonant background due to argon and the beams being overlapped in time. So the lower signal to noise ratio and the nonresonant contribution from argon make it appear much lower temperature. Another issue of these first tests was that beam overlap in the windows produced significant nonresonant background. This can actually be observed in the first 0.75 ms in figure 8.4



Figure 8.5. Fitted spectra versus time compared to the expected state temperatures

The following results and explanations were taken by Sean Kearney some weeks after the initial tests, once everything was well tuned. These are described and shown below. Results from a single- shock-tube operating condition are shown here. The driven-section gas in this case was pure N_2 . Nominal thermodynamic conditions were calculated from the measured speed of the Mach-6 incident shock wave, the known test-gas conditions, and real-gas expressions in the NASA equilibrium code and were: T1 = 292 K, P1 = 0.38 atm (unshocked N_2); T2 =2090 K, P2 = 1.1 atm (post incident shock); and T5 = 4013 K, P5 = 8.3 atm (post reflected shock). A spectrogram that reveals the time evolution of the measured single-laser-shot N_2 CARS spectra is shown in Figure 1. Demarcations in the data that clearly show the passage of incident (t = 140µs) and reflected (t = 180µs) shock waves and are marked by dashed white lines in the Figure. A third discontinuity in the spectrogram occurs near $t = 500\mu s$ and represents the arrival of compression waves reflected from the driver gas contact surface; the accompanying rise in pressure results in saturation of the CCD detector and represents the end of the experiment. Upon each successive demarcation, the bandwidth and the strength of the measured CARS signal increase, reflecting sudden increases in both temperature and pressure. The short, $40\mu s$ period between passage of the incident and reflected shocks was engineered to maximize the duration of the very high temperature T5 condition by using a long shock-tube end-wall insert, as the ability to measure temperatures in excess of 4000 K was of primary interest here.



Figure 8.6. Time/frequency spectrogram of the single-laser-pulse N_2 CARS intensity during a shock tube shot

Our single-laser-shot N_2 CARS spectra are background subtracted and normalized by burst-averaged nonresonant CARS spectra, acquired with argon in the test section approximately 15-20 minutes before the shock-tube firing, to account for the finite bandwidth of the Stokes pulse. Measured spectra are fit using a picosecond CARS model to be presented elsewhere. Two-dimensional libraries of spectra are parameterized by temperature and a scaling factor that accounts for the strength of the nonresonant CARS contribution. Pressure broadened Raman linewidths were calculated using the modified exponential gap (MEG) model for N_2 in the isolated-line approximation, with constants taken from Lavorel et al. The MEG model was necessarily extrapolated beyond flame temperatures, where it was developed, to reflected-shock temperatures in excess of T = 4000 K. The pressure was treated by generating three separate libraries at P1, P2, and P5 and fitting the data for each thermodynamic condition using the corresponding library spectra. P1 was fixed at the transducer-measured value of 0.38 atm; P2 was set to its equilibrium-calculated value of 1.1 atm; P5 was set to 10 atm, above its calculated value, to reflect the monotonic rise in pressure from 7.8 to 10.2 atm that was measured after the passage of the reflected shock. Representative fits to single-laser-shot data acquired under each of the three thermodynamic conditions are shown on the left-hand side of Figure 2. It should be mentioned that the nonresonant background is correlated with the temperature in the spectral fitting routine, which can introduce a source of bias into the CARS-measured temperatures. The nonresonant parameter was permitted to vary over a wide range when fitting spectra acquired under State-1 and State-2 conditions. An initial pass was performed on the State-5 data by varying both the temperature and nonresonant factor; this resulted in a wide range of fitted nonresonant values. For pure N_2 test gas with relatively low levels of dissociation, significant shot-to-shot variations in the nonresonant susceptibility are not physically realistic, and a second pass the with nonresonant parameter fixed at the average nonresonant factor of = 12 was used to obtain the State-5 temperature measurements presented here.



Figure 8.7. Representative fits to single laser shot (left), state averaged (center), and four-shot running average CARS measurements (right). Fitted values for the temperature and nonresonant background (α) are shown on the plots. The left and center columns reflect conditions that progress from State 1 to State 5 from top to bottom. The right-most column contains State 5 measurements only

The observed noise level in these single-shot data is higher than what is typically observed in N_2 CARS spectra obtained using nanosecond [164], [165] and femtosecond [136], [166], [167] pump and Stokes pulses. Our ~60-ps Stokes pulses with 100-120 cm^{-1} of bandwidth are ~450 × the Fourier-transform limit; as such, this represents an effectively chaotic laser source with random amplitude and phase jumps on the scale of a 150-fs coherence time that introduces a corresponding level of noise into the single-laser-shot CARS spectra. Femtosecond pulses are nearly Fourier-transform limited, providing a much more ideal Stokes source for CARS [166], [168]. Nanosecond Stokes pulses derived from broadband dye lasers have even lower coherence, but appear to offer better single-shot performance [164], [165], which we believe is due to a time-averaging effect over laser pulses that are several hundred Raman lifetimes in duration. In contrast, our picosecond pump and Stokes pulse durations are approximately 0.5-2 Raman lifetimes under the conditions encountered in these shock-tube experiments. Nevertheless, the State-2 and State-5 temperatures derived from fits to singlelaser-shot data are in reasonable agreement with the pre-shot calculations of T2 = 2090 K and T5 = 4013 K. The measured CARS spectra were additionally averaged over the duration of each thermodynamic state, and model fits with associated temperatures are shown in the center column of Figure 8.7. CARS-measured temperatures over the $500\mu s$ duration of the experiment are shown in Figure 3. All measurements represent single laser-shot realizations, with the exception of the maroon squares, which represent temperatures obtained from fits to a four-laser-shot moving average of the measured spectra. Sample fits to four-shot-average spectra acquired under State 5 conditions are shown in the right-hand column of Figure 8.7. State temperatures calculated from thermodynamic equilibrium are indicated by colored, dashed lines on the plot. A comparison between equilibrium calculated and mean CARSmeasured temperatures for each of the three thermodynamic states is provided in Table 1. At the coarse $2.5 cm^{-1}$ spectral resolution of this CARS instrument, the rotational structure in the low- temperature State-1 spectra is not resolved; low-temperature accuracy of the measurement suffers, with mean T1 that is 34% higher than the known pre-shot temperature. The State-2 mean temperature measurement improves to within 5.5% of the calculated T2 = 2090 K. Mean temperatures averaged over the duration of State 5 are 10.8% and 14% higher than the equilibrium value, for fits to single-laser-shot and four-shot-average spectra, respectively. Observation of the State-5 temperatures in Figure 3 indicate a systematic rise in temperature over the duration of this post-reflected- shock state. Initial post-reflectedshock temperatures for $t = 180 - 240 \mu s$ are generally in the 3900 K - 4070 K range for model fits to both single-laser-shot and 4-shot running average CARS spectra—values that are within 1.4-3% of the T5 equilibrium value. Beginning at $t = 250 \mu s$, CARS-measured temperatures begin to rise to a plateau near T = 4600-4800 K for $t = 300 - 420 \mu s$. This rise is consistent with an observed, gradual increase in the measured test-section pressure between the arrival of the reflected shock and any obvious effects associated with the contact surface. For $t > 450 \mu s$, there is a distinct rise in temperature to T ~5800 K, just prior to a significant increase in CARS signal strength associated with interaction of the test-section gas and the contact surface



Figure 8.8. Time-resolved CARS temperatures for a $500 - \mu s$ shock-tube event. The data are color coded according to the thermodynamic state delineated by the passage of incident and reflected shock waves. The legend indicates a fixed value of the pressure used to fit the measured spectra.

8.4 Summary and Conclusion

Picosecond burst-mode CARS of the N_2 molecule at 100-kHz laser repetition rate has been applied for time-resolution of the temperature history in an impulsive, $500\mu s$ duration shock-tube experiment.Single-shot CARS spectra at very high, T5 = 4000-5000 K, temperatures, and elevated pressures of P5 = 8-10.2 atm have been acquired with very high signal strength and analyzed for temperature measurements. Relative to nanosecond and femtosecond pump/Stokes Raman preparation, the measured spectra indicate an elevated level of noise, which we believe results from the combination of short picosecond pulse durations and poor coherence of the broadband picosecond Stokes source. Nevertheless, fits to the single-laser-shot spectra provide reasonable temperatures for post- incident (State-2) and post-reflected (State-5) conditions. Improved measurement fidelity was additionally demonstrated in the post-reflected-shock state by downgrading the effective acquisition rate from 100 to 25 kHz by implementing a four-shot running average of spectra. CARS spectra have been fit for temperature and a nonresonant background contribution, which is correlated to the resulting CARS temperature. Future experiments can be improved by reduction or elimination of the nonresonant CARS contribution using polarization or time-delayed probe-pulse schemes, which may introduce a challenging signal penalty. Introduction of burst-mode-pumped nanosecond Stokes sources [169] or femtosecond burst-mode lasers [112] will additionally improve the single-laser-shot precision of the measurements.

8.5 Acknowledgements

All the measurements were performed at Sandia, with a burst-mode pumped picosecond CARS system which they bought from Spectral Energies llc. and was built and installed by myself. I set up and ran the system for the first 5 shock tube runs. Following tests, including the one shown in figure 8.8 were performed by Sean Kearney and team.

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9. CONCLUSION

The purpose of this dissertation was to demonstrate the work and progress made in the advancement of various areas of Coherent Anti-Stokes Raman scattering as technique for gas-phase combustion diagnostics. The main advances are the creation of ERE-CARS for concentration measurements of formaldehyde, its validation, and application to high speed diagnostics, and 2) Development of the 100 kHz N_2 picosecond vibrational CARS measurement with the model validation, referencing and applications to challenging environments. Other minor contributions shown include the implementation and validation of a stable, extremely stable nanosecond CARS system for multi-species diagnostics.

9.1 Summary of Work

Quantitative ERE-CARS measurements of the CH_2O concentration were performed in a high-pressure mixing chamber and in a premixed DME/air flat-flame. Characterization data showed two close transitions in the $1_1^1 4_0^3$ vibronic transition band that could each provide electronic enhancement of the CARS signal mediated by the Raman-active ν_1 vibrational band of the ground electronic state. The measurements showed that the technique is effective at mole fractions lower than 55 parts per million of CH_2O in N_2 at 450 K, with an estimated detectability limit of 12 ppm. The quadratic dependence of the signal on the concentration was in agreement with expected CARS concentration dependence and was used as a calibration for experiments in a flame. The scaling of the signal with pressure also revealed transition line-broadening effects up to 11 bar. The pressure effects were apparent as low as 3 bar, but the signal increased with pressure-dependent number density up to 8 bar, above which it remained constant. Furthermore, application of the technique to a premixed dimethyl ether/air McKenna flat flame burner yielded a similar trend to that shown in previous literature, allowing additional characterization of the CH₂O concentration of this flame at varying heights and equivalence ratios with a precision of 11% or better. This was the first application of ERE-CARS measurements for CH₂O concentration, and the first application of a CARS technique to measure CH₂O concentration in a flame and in a high-pressure environment.

For high speed diagnostics a 100-kHz N_2 ps-VCARS system for accurate high-speed thermometry in turbulent reacting flows was developed and demonstrated. This was accomplished via a custom-built ps burst-mode OPG/OPA pumped at 355 nm, along with an efficient scheme for simultaneous NRB referencing. The system achieved an accuracy of 1.5% and precision of 4.7% in a steady adiabatic flame and was applied to two turbulent combustion environments, with the use of nitrogen being useful in a wide array of fuels and dynamic flames in practical combustion devices. A picosecond incoherent sum CARS model was developed, validated, and compared to current impulsive and time-independent models with the purpose of improving the picosecond CARS measurements. Further comparisons of the model for vibrational and rotational CARS yield interesting conclusions: for vibrational CARS there is a significant impact on the temperature accuracy when the incoherent sum model is used, while for rotational CARS measurements, the time-independent (nanosecond) model is very similar to the picosecond one in some cases. Furthermore, with the correct pulse parameters, the picosecond incoherent sum model can be extended to be used in the nanosecond and in the femtosecond regime. Computational time comparisons show that the model is 2-3 times slower than the hybrid fs/ps impulsive model.

100 kHz ps-CARS was first applied in laboratory Hencken type flames, then to a turbulent H_2/air jet, and to a DLR type A flame to measure temperature variations on the order of 100 kHz. The measurement was then applied to nitrocellulose and black powder fireballs to 1) find that it is possible to perform measurements in an O.D.~1 environment, and 2) that the temperature varies significantly depending on the location of the probe measurement volume compared to the burning particles within the fireball. Pyrometry was used at the same time as CARS to study the particle phase temperature, while CARS measured the gas phase temperature. Additional measurements in an e-match generated plasma created significant measurable non-equilibrium, indicating that with some improvements, the 100 kHz measurement may be used for non-equilibrium diagnostics.

100 kHz CARS measurements were also performed in the high-enthalpy Sandia free-piston shock tube. Due to the complexity of the environment, the measurement was performed without nonresonant background. Measurements of pre-shock, incident and reflected N_2 shocks could be taken with high enough measurement rate to provide insight into the ~ $500\mu s$ event. The range of temperatures measured went from 300 K, to ~5,000 K; which is extremely high temperature for measurements performed with CARS.

9.2 Future directions

In gas phase combustion, CARS concentration measurements in high pressure environments are currently of mild interest, because they would be used for more fundamental science and modeling, while current funding and excitement has significantly shifted in the U.S. to hypersonic flight and plasma assisted combustion. With this premise, CH_2O CARS remains now as a technique that can be leveraged for who is interested in fundamental combustion measurements, and high pressure models. Improvements upon the technique can be made by 1)shifting to stronger resonant transitions for a better electronic resonance enhancement, 2) Use of broadband dye laser to enable single shot mesurements, and 3) application of the technique with femtosecond lasers, in a similar fashion to the results shown by Stuffer et al for OH FREE(femtosecond fully resonant electrically enhanced) -CARS. A similar argument is valid for WIDECARS, although this technique is being currently used for measurements in some combustion environments of interest.

As mentioned, high speed diagnostics are currently a topic of much higher interest in the "gas-phase diagnostics" community. The interest of extending CARS to even higher repetition rates is high. Some improvements of the picosecond CARS system are possible, such as seeding of the OPG system with a separate light source, building a double pass OPG with separate idler, or taking steps to improve the M^2 of the beam entering the CARS system, as well as using better phase matching ad delay conditions for future experimental applications. I have already performed some tests in a H_2/air Hencken burner at 312.5 kHz with good SNR, as shown in fig. 9.1. With additional system improvements these measurements could be extended to application and the repetition rate further increased to > 500kHz. The resulting system could be even more stable, and used in additional field applications, with relative ease of setup (2-3 days).



Figure 9.1. Experimental data taken at 312.5 kHz in H_2/air Hencken burner for $\phi=1$

The main drawback that would not be easily improved on the current technique is the fact that the uncertainty will remain around 4-5% due to the inherent noise in the picosecond regime, even after all nonresonant referencing and corrections. If a lower uncertainty is required, it would be necessary to shift to a different time domain.

So, a major improvement would be to shift to nanosecond or femtosecond regimes The nanosecond regime is already being tested by [169] with some success, but will not overcome the known pressure scaling and nonresonant background issues of nanosecond CARS. Hybrid fs/ps CARS, instead is widely used at 1 kHz, has shown impressive accuracy and precision with < 1% uncertainty in some cases, and Smyser [112] has shown that there is promise for a burst-mode application of this, but there are many challenges in getting enough bandwidth and energy, as described in his publication. Another great improvement in recent years is the availability of high powered fiber femtosecond laser sources at an affordable cost (around \$50,000 which is reasonable compared to a few hudred thousand dollars for a kHz femtosecond laser, or a burst-mode laser). These laser sources can provide 50 fs pulses at 30-100 MHz repetition rate, generally at 780, 1040 or 1550 nm, and with energies from 5-120 nJ/pulse. Use of one of these fiber lasers could provide a good seed source for a burst-mode pumped optical parametric amplification system, as shown in the schematic below in figure 9.2. The key to burst-mode hybrid fs/ps CARS, similarly to ps-CARS, is to produce a stokes (or pump/stokes) broadband bandwidth limited beam, as the probe can already be readily obtained from the SHG output of the burst-mode laser. Requirements for the pump/stokes output are a bare minimum of ~ 10J, and ideally ~ 100 μJ (add references). This can almost be obtained with a simple OPA setup: assuming 100 nJ fiber laser output pulses an AOM can be used to redirect one every 80 into the burst mode laser. The pulse would be spectrally filtered to create a 10-100 ps $\sim 0.5 - 1nJ$ pulse, which is sufficient for providing a a 1 MHz seed to the burst-mode. If needed, this pulse can be passed through a fiber amplifier, and AOM or EOM to further reduce the repetition rate. At 100 kHz rep. rate one may expect 50 ps 532 nm pulses with at least 50 mJ/pulse. A small fraction of the output can be used for the probe pulse, which needs to be 1-2 mJ, while the rest can be used to pump OPA stages to amplify the 100 nJ femtosecond pulse. Because The next pulse after the one picked off for the burst mode, will arrive 12.5 ns later, corresponding to an optical path length of 3.75 m; the two pulses will always overlap at the OPA provided that the path length is adjusted correctly. As mentioned previously, OPA amplification can be achieved with up to 20%conversion efficiency. The temporal energy density of the 50 ps pulses would be $1\mu J/fs$, or ~ 120 over the 120 fs pulse width. The best case scenario would provide $24\mu J$ stokes pulses, wasting almost all of the potential pump energy. This can be overcome by stretching the 120 fs pulse to picoseconds, and then re-compressing it after noncolinear chirped pulse amplification^[170], a commonly used technique for high energy femtosecond pulse amplification.



Figure 9.2. Schematic of possible arrangement to produce pulses for hybrid fs/ps rotational CARS

While there will be challenges, building a stable burst-mode hybrid fs/ps CARS system would result in low uncertainty rotational CARS temperature measurements which could be applied at high repetition rates. If such a system could then provide mJ pump/stokes energies at kHz rates, applications such as splitting the output into multiple pulses (minibursts) to track the temperature in plasma discharges at $\sim 0.1 - 1$ ns time intervals, or use the excess energy for multi-point CARS measurements.

More immediate applications would be extensions of what is already achievable with the developed hundred kHz picosecond CARS system: measuring temperature in low pressure wind tunnels, rotating detonation engines, energetic materials events, detonations.

To conclude, I see two paths for the future for high-speed CARS:

1) The first is to further develop the current ps-CARS system: make it so that alignment and setup requirements are minimal, have software to analyse the data immediately. Then actually use it as a tool for diagnostics which can be moved, and used in different locations and labs. This may be as a more commercial aspect, but is extremely important, as too often these diagnostics end up being used almost solely for demonstration purposes.

2) More on the research side: leverage the developments from ps-CARS to build a hybrid fs/ps CARS system as described above, with the possibility that it will take time to solve development challenges and obtain a stable system, comparable to, and then better than, the 100 kHz N_2 ps-CARS.

REFERENCES

- K. D. Rein, S. Roy, S. T. Sanders, A. W. Caswell, F. R. Schauer, and J. R. Gord, "Measurements of gas temperatures at 100 kHz within the annulus of a rotating detonation engine," *Applied Physics B: Lasers and Optics*, vol. 123, no. 3, pp. 1–9, 2017, ISSN: 09462171. DOI: 10.1007/s00340-017-6647-5.
- [2] D. Lauriola, T. Meyer, M. Gomez, S. Roy, M. Slipchenko, J. Gord, and S. Son, "KHz-MHz Rate laser-based tracking of particles and product gases for multiphase blast fields," in *RAPID 2018 - 2018 IEEE Research and Applications of Photonics In Defense Conference*, 2018, ISBN: 9781538653494. DOI: 10.1109/RAPID.2018.8508993.
- [3] D. Lauriola, M. Gomez, T. Meyer, S. Son, M. Slipchenko, and S. Roy, "High-speed particle image velocimetry and particle tracking methods in reactive and non-reactive flows," in AIAA Scitech 2019 Forum, 2019, ISBN: 9781624105784. DOI: 10.2514/6. 2019-1605.
- [4] A. Farooq, J. B. Jeffries, and R. K. Hanson, "Sensitive detection of temperature behind reflected shock waves using wavelength modulation spectroscopy of CO2 near 2.7 μm," Applied Physics B: Lasers and Optics, vol. 96, no. 1, pp. 161–173, 2009, ISSN: 09462171. DOI: 10.1007/s00340-009-3446-7.
- [5] C. Winters, T. Haller, S. Kearney, P. Varghese, K. Daniel, J. Wagner, C. A. Winters, T. I. Haller, S. E. A. N. Kearney, P. H. Varghese, K. Y. L. E. L. Ynch, K. Y. L. E. D. Aniel, and J. U. Wagner, "Pulse-Burst Spontaneous Raman Thermometry of Unsteady Wave Phenomena in a Shock Tube," 2021.
- [6] P. R. Régnier and J. P. Taran, "On the possibility of measuring gas concentrations by stimulated anti-Stokes scattering," *Applied Physics Letters*, vol. 23, no. 5, pp. 240– 242, 1973, ISSN: 00036951. DOI: 10.1063/1.1654873.
- [7] J. A. Shirley, R. J. Hall, and A. C. Eckbreth, "Folded BOXCARS for rotational Raman studies," *Optics Letters*, vol. 5, no. 9, p. 380, 1980, ISSN: 0146-9592. DOI: 10.1364/ol.5.000380.
- [8] B. Attal, D. Débarre, K. Müller-Dethlefs, and J. Taran, "Resonance-enhanced coherent anti-Stokes Raman scattering in C2," *Revue de Physique Appliquée*, vol. 18, no. 1, pp. 39–50, 1983, ISSN: 0035-1687. DOI: 10.1051/rphysap:0198300180103900.
- [9] J. P. Haushalter and M. D. Morris, "Excitation Frequency Dependence of Resonance-Enhanced Inverse Raman Band Shapes," *Analytical Chemistry*, vol. 53, no. 1, pp. 21– 25, 1981, ISSN: 15206882. DOI: 10.1021/ac00224a008.

- [10] N. Chai, W. D. Kulatilaka, S. V. Naik, N. M. Laurendeau, R. P. Lucht, J. P. Kuehner, S. Roy, V. R. Katta, and J. R. Gord, "Nitric oxide concentration measurements in atmospheric pressure flames using electronic-resonance-enhanced coherent anti-Stokes Raman scattering," *Applied Physics B: Lasers and Optics*, vol. 88, no. 1, pp. 141–150, 2007, ISSN: 09462171. DOI: 10.1007/s00340-007-2647-1.
- [11] S. P. Kearney, D. J. Scoglietti, and C. J. Kliewer, "Hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering temperature and concentration measurements using two different picosecond-duration probes," *Optics Express*, vol. 21, no. 10, p. 12327, 2013, ISSN: 1094-4087. DOI: 10.1364/oe.21.012327.
- [12] S. Roy, J. R. Gord, and A. K. Patnaik, "Recent advances in coherent anti-Stokes Raman scattering spectroscopy: Fundamental developments and applications in reacting flows," *Progress in Energy and Combustion Science*, vol. 36, no. 2, pp. 280– 306, 2010, ISSN: 03601285. DOI: 10.1016/j.pecs.2009.11.001. [Online]. Available: http://dx.doi.org/10.1016/j.pecs.2009.11.001.
- H. U. Stauffer, K. A. Rahman, M. N. Slipchenko, S. Roy, J. R. Gord, and T. R. Meyer, "Interference-free hybrid fs/ps vibrational CARS thermometry in high-pressure flames," *Optics Letters*, vol. 43, no. 20, p. 4911, 2018, ISSN: 0146-9592. DOI: 10.1364/ol.43. 004911.
- S. P. Kearney, K. Frederickson, and T. W. Grasser, "Dual-pump coherent anti-Stokes Raman scattering thermometry in a sooting turbulent pool fire," *Proceedings of the Combustion Institute*, vol. 32 I, no. 1, pp. 871–878, 2009, ISSN: 15407489. DOI: 10. 1016/j.proci.2008.06.148. [Online]. Available: http://dx.doi.org/10.1016/j.proci.2008. 06.148.
- [15] V. Athmanathan, K. A. Rahman, D. K. Lauriola, J. Braun, G. Paniagua, M. N. Slipchenko, S. Roy, and T. R. Meyer, "Femtosecond/picosecond rotational coherent anti-Stokes Raman scattering thermometry in the exhaust of a rotating detonation combustor," *Combustion and Flame*, 2021.
- [16] D. K. Lauriola, K. A. Rahman, H. U. Stauffer, M. N. Slipchenko, T. R. Meyer, and S. Roy, "Concentration and pressure scaling of CH 2 O electronic-resonance-enhanced coherent anti-Stokes Raman scattering signals," *Applied Optics*, vol. 60, no. 4, p. 1051, 2021, ISSN: 1559-128X. DOI: 10.1364/ao.415496.
- [17] N. Rock, P. S. Hsu, D. Lauriola, N. Rahman, J. Estevadeordal, S. W. Grib, N. Jiang, S. P. Kearney, and P. Wrzesinski, "WIDECARS multi-parameter measurements in premixed ethylene–air flames using a wavelength stable ultrabroadband dye laser," *Applied Optics*, vol. 59, no. 8, p. 2649, Mar. 2020, ISSN: 1559-128X. DOI: 10.1364/ao. 386378.

- [18] Z. Wang, P. Stamatoglou, M. Lundgren, L. Luise, B. M. Vaglieco, A. Andersson, M. Aldén, Ö. Andersson, and M. Richter, "Simultaneous 36 kHz PLIF/chemiluminescence imaging of fuel, CH 2 O and combustion in a PPC engine," *Proceedings of* the Combustion Institute, vol. 37, no. 4, pp. 4751–4758, 2019, ISSN: 15407489. DOI: 10.1016/j.proci.2018.06.019. [Online]. Available: https://doi.org/10.1016/j.proci. 2018.06.019.
- [19] D. K. Lauriola, P. S. Hsu, N. Jiang, M. N. Slipchenko, T. R. Meyer, and S. Roy, " Burst-mode 100 kHz N 2 ps-CARS flame thermometry with concurrent nonresonant background referencing," *Optics Letters*, vol. 46, no. 21, p. 5489, 2021, ISSN: 0146-9592. DOI: 10.1364/ol.439996.
- [20] D. K. Lauriola, A. D. Brown, P. Hsu, N. Jiang, S. Roy, T. R. Meyer, and S. F. Son, "100 kHz burst-mode picosecond vibrational N 2 CARS thermometry in energetic combustion environments," in AIAA Scitech 2022 Forum, 2022, pp. 1–9. DOI: 10. 2514/6.2022-1943.
- [21] T. Haiman, "Stimulated Optical Radiation in Ruby," *Nature*, vol. 187, 1960.
- [22] M. Schwar and F. Weinberg, "Laser techniques in combustion research," Combustion and Flame, vol. 13, no. 4, 1969.
- [23] L. M. Fraser and J. Winefordner, "Laser-Excited Atomic Fluorescence Flame Spectrometry," *Analytical Chemistry*, vol. 43, no. 12, pp. 1693–1696, 1971, ISSN: 15206882. DOI: 10.1021/ac00034a001.
- [24] M. C. Drake and G. M. Rosenblatt, "FLAME TEMPERATURES FROM RAMAN SCATTERING," *Chemical Physics Letters*, vol. 44, no. 2, pp. 313–316, 1976.
- [25] R. W. Pitz, R. Cattolica, F. Robben, and L. Talbot, "Temperature and density in a hydrogenair flame from Rayleigh scattering," *Combustion and Flame*, vol. 27, no. C, pp. 313–320, 1976, ISSN: 00102180. DOI: 10.1016/0010-2180(76)90036-5.
- [26] M. A. Yuratich, "Effects of laser linewidth on coherent antistokes Raman spectroscopy," *Molecular Physics*, vol. 38, no. 2, pp. 625–655, 1979, ISSN: 13623028. DOI: 10.1080/ 00268977900101941.
- [27] S. A. Druet, B. Attal, T. K. Gustafson, and J. P. Taran, "Electronic resonance enhancement of coherent anti-Stokes Raman scattering," *Physical Review A*, vol. 18, no. 4, pp. 1529–1557, 1978, ISSN: 10502947. DOI: 10.1103/PhysRevA.18.1529.

- [28] E. C. Tuazon, A. M. Winer, and J. N. Pitts, "Trace Pollutant Concentrations in a Multiday Smog Episode in the California South Coast Air Basin by Long Path Length Fourier Transform Infrared Spectroscopy," *Environmental Science and Technology*, vol. 15, no. 10, pp. 1232–1237, 1981, ISSN: 15205851. DOI: 10.1021/es00092a014.
- [29] G. Magnotti, K. C. Utsav, P. L. Varghese, and R. S. Barlow, "Raman spectra of methane, ethylene, ethane, dimethyl ether, formaldehyde and propane for combustion applications," *Journal of Quantitative Spectroscopy and Radiative Transfer*, vol. 163, pp. 80–101, 2015, ISSN: 00224073. DOI: 10.1016/j.jqsrt.2015.04.018.
- [30] Z. Wang, P. Stamatoglou, Z. Li, M. Aldén, and M. Richter, "Ultra-high-speed PLIF imaging for simultaneous visualization of multiple species in turbulent flames," *Optics Express*, vol. 25, no. 24, p. 30214, 2017, ISSN: 1094-4087. DOI: 10.1364/oe.25.030214.
- [31] S. W. Grib, N. Jiang, P. S. Hsu, P. M. Danehy, and S. Roy, "Rayleigh-scattering-based two-dimensional temperature measurement at 100-kHz frequency in a reacting flow," *Optics Express*, vol. 27, no. 20, p. 27 902, 2019, ISSN: 1094-4087. DOI: 10.1364/oe.27. 027902.
- [32] R. L. Gordon, A. R. Masri, and E. Mastorakos, "Simultaneous Rayleigh temperature, OH- and CH2O-LIF imaging of methane jets in a vitiated coflow," *Combustion* and Flame, vol. 155, no. 1-2, pp. 181–195, 2008, ISSN: 00102180. DOI: 10.1016/j. combustflame.2008.07.001. [Online]. Available: http://dx.doi.org/10.1016/j. combustflame.2008.07.001.
- [33] Y. C. Mazumdar, M. E. Smyser, J. D. Heyborne, M. N. Slipchenko, and D. R. Guildenbecher, "Megahertz-rate shock-wave distortion cancellation via phase conjugate digital in-line holography," *Nature Communications*, vol. 11, no. 1, pp. 1–10, 2020, ISSN: 20411723. DOI: 10.1038/s41467-020-14868-y. [Online]. Available: http://dx.doi.org/10.1038/s41467-020-14868-y.
- [34] B. R. Halls, N. Jiang, T. R. Meyer, S. Roy, M. N. Slipchenko, and J. R. Gord, "4D spatiotemporal evolution of combustion intermediates in turbulent flames using burst-mode volumetric laser-induced fluorescence," *Optics Letters*, vol. 42, no. 14, p. 2830, 2017, ISSN: 0146-9592. DOI: 10.1364/ol.42.002830.
- [35] M. N. Slipchenko, T. R. Meyer, and S. Roy, "Advances in burst-mode laser diagnostics for reacting and nonreacting flows," *Proceedings of the Combustion Institute*, vol. 38, p. 1533, 2020, ISSN: 15407489. DOI: 10.1016/j.proci.2020.07.024. [Online]. Available: https://doi.org/10.1016/j.proci.2020.07.024.

- [36] K. O. Winter and M. J. Hargather, "Three-dimensional shock wave reconstruction using multiple high-speed digital cameras and background-oriented schlieren imaging," *Experiments in Fluids*, vol. 60, no. 6, pp. 1–13, 2019, ISSN: 14321114. DOI: 10.1007/s00348-019-2738-x. [Online]. Available: https://doi.org/10.1007/s00348-019-2738-x.
- [37] C. M. Jenkins, Y. Horie, and C. Y. Wu, "Particle velocity and structures in blast waves imaged using particle image velocimetry," in *International Journal of Multiphase Flow*, vol. 36, Jan. 2010, pp. 88–91. DOI: 10.1016/J.IJMULTIPHASEFLOW.2009.08. 004.
- [38] A. N. Leidy, I. T. Neel, N. R. Tichenor, and R. D. Bowersox, "High-speed schlieren imaging of cylinder-induced hypersonic-shock-wave-boundary-layer interactions," *AIAA Journal*, vol. 58, no. 7, pp. 3090–3099, 2020, ISSN: 00011452. DOI: 10.2514/1.J059193.
- [39] S. A. Skeen, J. Manin, and L. M. Pickett, "Simultaneous formaldehyde PLIF and high-speed schlieren imaging for ignition visualization in high-pressure spray flames," *Proceedings of the Combustion Institute*, 2015, ISSN: 15407489. DOI: 10.1016/j.proci. 2014.06.040.
- [40] Y. Gao, X. Yang, C. Fu, Y. Yang, Z. Li, H. Zhang, and F. Qi, "10 kHz simultaneous PIV/PLIF study of the diffusion flame response to periodic acoustic forcing," eng, *Applied Optics*, vol. 58, no. 10, p. C112, 2019, ISSN: 1559-128X. DOI: 10.1364/ao.58. 00c112.
- [41] B. Thurow, N. Jiang, and W. Lempert, "Review of ultra-high repetition rate laser diagnostics for fluid dynamic measurements," *Measurement Science and Technology*, vol. 24, no. 1, 2013, ISSN: 13616501. DOI: 10.1088/0957-0233/24/1/012002.
- [42] C. A. Fugger, S. Roy, A. W. Caswell, B. A. Rankin, and J. R. Gord, "Structure and dynamics of CH2O, OH, and the velocity field of a confined bluff-body premixed flame, using simultaneous PLIF and PIV at 10kHz.," *Proceedings of the Combustion Institute*, vol. 37, no. 2, pp. 1461–1469, 2019, ISSN: 15407489. DOI: 10.1016/j.proci. 2018.05.014. [Online]. Available: https://doi.org/10.1016/j.proci.2018.05.014.
- [43] F. Qi, X. Liu, Y. Wang, and Z. Wang, "Single camera 20 kHz two-color formalde-hyde PLIF thermometry using a dual-wavelength-switching burst mode laser," Optics Letters, Vol. 46, Issue 20, pp. 5149-5152, vol. 46, no. 20, pp. 5149–5152, Oct. 2021, ISSN: 1539-4794. DOI: 10.1364/OL.439735. [Online]. Available: https://www.osapublishing.org/viewmedia.cfm?uri=ol-46-20-5149&seq=0&html=true%20https://www.osapublishing.org/abstract.cfm?uri=ol-46-20-5149%20https://www.osapublishing.org/ol/abstract.cfm?uri=ol-46-20-5149.

- [44] N. Jiang, M. Webster, W. R. Lempert, J. D. Miller, T. R. Meyer, C. B. Ivey, and P. M. Danehy, "MHz-rate nitric oxide planar laser-induced fluorescence imaging in a Mach 10 hypersonic wind tunnel," *Applied Optics*, vol. 50, no. 4, 2011, ISSN: 15394522. DOI: 10.1364/AO.50.000A20.
- [45] K. N. Gabet, R. A. Patton, N. Jiang, W. R. Lempert, and J. A. Sutton, "High-speed CH 2O PLIF imaging in turbulent flames using a pulse-burst laser system," *Applied Physics B: Lasers and Optics*, vol. 106, no. 3, pp. 569–575, 2012, ISSN: 09462171. DOI: 10.1007/s00340-012-4881-4.
- [46] A. P. Nair, D. D. Lee, D. I. Pineda, J. Kriesel, W. A. Hargus, J. W. Bennewitz, S. A. Danczyk, and R. M. Spearrin, *MHz laser absorption spectroscopy via diplexed RF modulation for pressure, temperature, and species in rotating detonation rocket flows*, 2020. DOI: 10.1007/s00340-020-07483-8.
- [47] A. Gratien, B. Picquet-Varrault, J. Orphal, E. Perraudin, J. F. Doussin, and J. M. Flaud, "Laboratory intercomparison of the formaldehyde absorption cross sections in the infrared (1660-1820 cm-1) and ultraviolet (300-360 nm) spectral regions," *Journal of Geophysical Research Atmospheres*, vol. 112, no. 5, pp. 1–10, 2007, ISSN: 01480227. DOI: 10.1029/2006JD007201.
- [48] C. Ernest, "High-Resolution Studies of the $\tilde{A}^1A X^{-1}A$ Electronic Transition of Formaldehyde : Spectroscopy and Photochemistry," PhD thesis, 2017.
- [49] B. Attal-Trétout, S. C. Schmidt, E. Crété, P. Dumas, and J. P. Taran, "Resonance cars of OH in high-pressure flames," *Journal of Quantitative Spectroscopy and Radiative Transfer*, vol. 43, no. 5, pp. 351–364, 1990, ISSN: 00224073. DOI: 10.1016/0022-4073(90)90001-M.
- [50] H. U. Stauffer, S. Roy, J. B. Schmidt, P. J. Wrzesinski, and J. R. Gord, "Two-color vibrational, femtosecond, fully resonant electronically enhanced CARS (FREE-CARS) of gas-phase nitric oxide," *Journal of Chemical Physics*, vol. 145, no. 12, 2016, ISSN: 00219606. DOI: 10.1063/1.4962834.
- [51] P. J. Wrzesinski, H. U. Stauffer, J. B. Schmidt, S. Roy, and J. R. Gord, "Femtosecond fully resonant electronically enhanced CARS (FREE-CARS) for simultaneous minor-species detection and single-shot thermometry," *Optics Letters*, vol. 41, no. 9, pp. 2021–2024, 2016. DOI: 10.1364/UP.2016.UM2A.1.
- [52] T. R. Meyer, S. Roy, R. P. Lucht, and J. R. Gord, "Dual-pump dual-broadband CARS for exhaust-gas temperature and CO 2-O2-N2 mole-fraction measurements in model gas-turbine combustors," *Combustion and Flame*, vol. 142, no. 1-2, pp. 52–61, 2005, ISSN: 00102180. DOI: 10.1016/j.combustflame.2005.02.007.

- [53] P. Maker and R. Terhune, "Study of optical effects due to an Induced Polarization Third Order in the Elecric Field Strength," *Physical Review A*, vol. 137, no. 3, pp. 801– 818, 1965.
- [54] S. F. Hanna, W. D. Kulatilaka, Z. Arp, T. Opatrný, M. O. Scully, J. P. Kuehner, and R. P. Lucht, "Electronic-resonance-enhanced coherent anti-Stokes Raman spectroscopy of nitric oxide," *Applied Physics Letters*, vol. 83, no. 9, pp. 1887–1889, 2003, ISSN: 00036951. DOI: 10.1063/1.1604947.
- [55] W. D. Kulatilaka, N. Chai, S. V. Naik, S. Roy, N. M. Laurendeau, R. P. Lucht, J. P. Kuehner, and J. R. Gord, "Effects of pressure variations on electronic-resonance-enhanced coherent anti-Stokes Raman scattering of nitric oxide," *Optics Communications*, vol. 274, no. 2, pp. 441–446, 2007, ISSN: 00304018. DOI: 10.1016/j.optcom. 2007.02.022.
- [56] M. Bruchhausen, J. Voigt, T. Doerk, S. Hädrich, and J. Uhlenbusch, "Resonant coherent anti-stokes raman scattering applied to vapor phase InI," *Journal of Molecular Spectroscopy*, vol. 201, no. 1, pp. 70–82, 2000, ISSN: 00222852. DOI: 10.1006/jmsp. 2000.8069.
- [57] B. Hudson, W. Hetherington, S. Cramer, I. Chabay, and G. K. Klauminzer, "Resonance enhanced coherent anti-Stokes Raman scattering.," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 73, no. 11, pp. 3798–3802, 1976, ISSN: 00278424. DOI: 10.1073/pnas.73.11.3798.
- [58] T. Doerk, P. Jauernik, S. Hädrich, B. Pfelzer, and J. Uhlenbusch, "Resonance enhanced CARS applied to the CH radical," *Optics Communications*, vol. 118, no. 5-6, pp. 637–647, 1995, ISSN: 00304018. DOI: 10.1016/0030-4018(95)00304-Q.
- [59] A. Pott, T. Doerk, J. Uhlenbusch, J. Ehlbeck, J. Höschele, and J. Steinwandel, "Polarization-sensitive coherent anti-Stokes Raman scattering applied to the detection of NO in a microwave discharge for reduction of NO," *Journal of Physics D: Applied Physics*, vol. 31, no. 19, pp. 2485–2498, 1998, ISSN: 00223727. DOI: 10.1088/0022-3727/31/19/020.
- [60] N. Chai, S. V. Naik, W. D. Kulatilaka, N. M. Laurendeau, R. P. Lucht, S. Roy, and J. R. Gord, "Detection of acetylene by electronic resonance-enhanced coherent anti-Stokes Raman scattering," *Applied Physics B: Lasers and Optics*, vol. 87, no. 4, pp. 731–737, 2007, ISSN: 09462171. DOI: 10.1007/s00340-007-2650-6.
- [61] P. He, R. W. Fan, Y. Q. Xia, X. Yu, Y. Yao, and D. Y. Chen, "Femtosecond timeresolved resonance-enhanced CARS of gaseous iodine at room temperature," *Chinese Physics Letters*, vol. 28, no. 4, pp. 1–5, 2011, ISSN: 0256307X. DOI: 10.1088/0256-307X/28/4/047804.

- [62] H. U. Stauffer, J. D. Miller, M. N. Slipchenko, T. R. Meyer, B. D. Prince, S. Roy, and J. R. Gord, "Time- and frequency-dependent model of time-resolved coherent anti-Stokes Raman scattering (CARS) with a picosecond-duration probe pulse," *The Journal of Chemical Physics*, vol. 140, no. 2, p. 024316, Jan. 2014, ISSN: 0021-9606. DOI: 10.1063/1.4860475. [Online]. Available: http://aip.scitation.org/doi/10.1063/1. 4860475.
- [63] D. R. Richardson, S. P. Kearney, and D. R. Guildenbecher, "Post-detonation fireball thermometry via femtosecond-picosecond coherent anti-Stokes Raman Scattering (CARS)," *Proceedings of the Combustion Institute*, vol. 000, pp. 1–8, 2020, ISSN: 15407489. DOI: 10.1016/j.proci.2020.06.257.
- [64] P. Beaud, H. Frey, T. Lang, and M. Motzkus, "Flame thermometry by femtosecond CARS," *Chemical Physics Letters*, vol. 344, no. August, pp. 407–412, 2001.
- [65] T. R. Meyer, S. Roy, and J. R. Gord, "Improving signal-to-interference ratio in rich hydrocarbon-air flames using picosecond coherent anti-stokes raman scattering," *Applied Spectroscopy*, vol. 61, no. 11, pp. 1135–1140, 2007, ISSN: 00037028. DOI: 10.1366/ 000370207782596996.
- [66] A. Montello, M. Nishihara, J. W. Rich, I. V. Adamovich, and W. R. Lempert, "Picosecond USED-CARS for simultaneous rotational/translational and vibrational temperature measurement of Nitrogen in a nonequilibrium mach 5 flow," 50th AIAA Aerospace Sciences Meeting Including the New Horizons Forum and Aerospace Exposition, no. January, pp. 1–31, 2012. DOI: 10.2514/6.2012-239.
- [67] D. Escofet-Martin, A. O. Ojo, J. Collins, N. T. Mecker, M. Linne, and B. Peterson, " Dual-probe 1D hybrid fs/ps rotational CARS for simultaneous single-shot temperature, pressure, and O 2 /N 2 measurements," *Optics Letters*, vol. 45, no. 17, p. 4758, 2020, ISSN: 0146-9592. DOI: 10.1364/ol.400595.
- [68] S. P. Kearney, D. R. Richardson, J. E. Retter, and P. M. Danehy, "Simultaneous Temperature/Pressure Monitoring in Compressible Flows using Hybrid fs/ps Pure-Rotational CARS," in AIAA Scitech 2020 Forum, 2020.
- [69] M. A. Yuratich and D. C. Hanna, "Nonlinear atomic susceptibilities," Journal of Physics B: Atomic and Molecular Physics, vol. 9, no. 5, pp. 729–750, 1976, ISSN: 00223700. DOI: 10.1088/0022-3700/9/5/017.
- [70] A. C. Eckbreth, Laser Diagnostics for Combustion Temperature and Species, C. Press, Ed. 1996.
- [71] D. Lauriola, "Laser filamentation in air and glass," Tech. Rep., 2021, pp. 5–6.

- [72] A. Perosa, M. Selva, V. Lucchini, M. Fabris, and M. Noè, "Kinetic parameter estimation of solvent-free reactions monitored by 13C NMR spectroscopy, a case study: Mono- and di-(hydroxy)ethylation of aniline with ethylene carbonate," *International Journal of Chemical Kinetics*, vol. 43, no. 3, pp. 154–160, 2011, ISSN: 1097-4601. DOI: 10.1002/kin. [Online]. Available: http://dx.doi.org/10.1002/kin.20532.
- [73] J. Vandooren, L. O. de Guertechin, and P. J. Van Tiggelen, "Kinetics in a lean formaldehyde flame," *Combustion and Flame*, vol. 64, no. 2, pp. 127–139, 1986, ISSN: 00102180. DOI: 10.1016/0010-2180(86)90050-7.
- [74] A. Rodriguez, O. Frottier, O. Herbinet, R. Fournet, R. Bounaceur, C. Fittschen, and F. Battin-Leclerc, "Experimental and Modeling Investigation of the Low-Temperature Oxidation of Dimethyl Ether," *Journal of Physical Chemistry A*, vol. 119, no. 28, pp. 7905–7923, 2015, ISSN: 15205215. DOI: 10.1021/acs.jpca.5b01939.
- [75] C. A. Idicheria and L. M. Pickett, "Formaldehyde visualization near lift-off location in a diesel jet," *SAE Technical Papers*, 2006, ISSN: 26883627. DOI: 10.4271/2006-01-3434.
- [76] K. Cung, X. Zhu, A. A. Moiz, S. Y. Lee, and W. De Ojeda, "Characteristics of Formaldehyde (CH2O) Formation in Dimethyl Ether (DME) Spray Combustion Using PLIF Imaging," SAE International Journal of Fuels and Lubricants, vol. 9, no. 1, pp. 138–148, 2016, ISSN: 19463960. DOI: 10.4271/2016-01-0864.
- [77] J. Wang, M. Chaos, B. Yang, T. A. Cool, F. L. Dryer, T. Kasper, N. Hansen, P. Oßwald, K. Kohse-Höinghaus, and P. R. Westmoreland, "Composition of reaction intermediates for stoichiometric and fuel-rich dimethyl ether flames: Flame-sampling mass spectrometry and modeling studies," *Physical Chemistry Chemical Physics*, vol. 11, no. 9, pp. 1328–1339, 2009, ISSN: 14639076. DOI: 10.1039/b815988b.
- [78] D. M. Smith, "Vibration-rotation interactions between overtone and combination levels of asymmetric-top molecules: Application to the infrared spectroscopy of formaldehyde and ketene," *Journal of Chemical Physics*, vol. 122, no. 3, 2005, ISSN: 00219606. DOI: 10.1063/1.1835263.
- [79] D. C. Moule and A. D. Walsh, "Ultraviolet Spectra and Excited States of Formaldehyde," *Chemical Reviews*, vol. 75, no. 1, pp. 67–84, 1975, ISSN: 15206890. DOI: 10. 1021/cr60293a003.
- [80] A. M. Walser, M. Meisinger, P. P. Radi, T. Gerber, and G. Knopp, "Resonant UVfs-TCFWM spectroscopy on formaldehyde," *Physical Chemistry Chemical Physics*, vol. 11, no. 38, pp. 8456–8466, 2009, ISSN: 14639076. DOI: 10.1039/b907133d.

- [81] E. W. Kaiser, T. J. Wallington, M. D. Hurley, J. Platz, H. J. Curran, W. J. Pitz, and C. K. Westbrook, "Experimental and modeling study of premixed atmosphericpressure dimethyl ether - air flames," *Journal of Physical Chemistry A*, vol. 104, no. 35, pp. 8194–8206, 2000, ISSN: 10895639. DOI: 10.1021/jp994074c.
- [82] J. B. Michael, P. Venkateswaran, J. D. Miller, M. N. Slipchenko, J. R. Gord, S. Roy, and T. R. Meyer, "100 kHz thousand-frame burst-mode Imaging in Turbulent Flames," *Optics L*, vol. 39, no. 4, pp. 3–6, 2014.
- [83] U. Retzer, R. Pan, T. Werblinski, F. J. T. Huber, M. N. Slipchenko, T. R. Meyer, L. Zigan, and S. Will, "Burst-mode OH/CH 2 O planar laser-induced fluorescence imaging of the heat release zone in an unsteady flame," *Optics Express*, vol. 26, no. 14, p. 18105, 2018, ISSN: 1094-4087. DOI: 10.1364/oe.26.018105.
- [84] K. Y. Cho, C. A. Fugger, R. T. Fievisohn, B. C. Sell, J. L. Hoke, S. P. Kearney, A. W. Caswell, J. R. Gord, and F. R. Schauer, "Burst-mode 355 nm plif for detonation wave front visualization and 100–300 khz particle image velocimetry," *AIAA Scitech 2019 Forum*, no. January, pp. 1–13, 2019. DOI: 10.2514/6.2019-2249.
- [85] J. D. Miller, S. J. Peltier, M. N. Slipchenko, J. G. Mance, T. M. Ombrello, J. R. Gord, and C. D. Carter, "Investigation of transient ignition processes in a model scramjet pilot cavity using simultaneous 100 kHz formaldehyde planar laser-induced fluorescence and CH* chemiluminescence imaging," *Proceedings of the Combustion Institute*, vol. 36, no. 2, pp. 2865–2872, 2017, ISSN: 15407489. DOI: 10.1016/j.proci. 2016.07.060. [Online]. Available: http://dx.doi.org/10.1016/j.proci.2016.07.060.
- [87] W. D. Kulatilaka, N. Chai, S. V. Naik, N. M. Laurendeau, R. P. Lucht, J. P. Kuehner, S. Roy, and J. R. Gord, "Measurement of nitric oxide concentrations in flames by using electronic-resonance-enhanced coherent anti-Stokes Raman scattering," *Optics Letters*, vol. 31, no. 22, p. 3357, 2006, ISSN: 0146-9592. DOI: 10.1364/ol.31.003357.
- [88] A. M. Walser, "Time-Resolved Four-Wave Mixing Spectroscopy of Gaseous Formaldehyde," *Molecules*, no. 18044, p. 174, 2008. DOI: 10.3929/ethz-a-005740419.

- [89] M. Tulej, M. Meisinger, G. Knopp, A. M. Walser, P. Beaud, T. Gerber, and P. P. Radi, "Degenerate and two-color resonant four-wave mixing applied to the rotational characterization of high-lying vibrational states of formaldehyde (Ã, 1A 2)," *Journal of Raman Spectroscopy*, vol. 37, no. 1-3, pp. 376–383, 2006, ISSN: 03770486. DOI: 10.1002/jrs.1438.
- [90] D. J. Clouthier and D. A. Ramsay, "The Spectroscopy of Formaldehyde and Thioformaldehyde," Annual Review of Physical Chemistry, vol. 34, no. 1, pp. 31–58, 1983, ISSN: 0066-426X. DOI: 10.1146/annurev.pc.34.100183.000335.
- [91] R. J. Bouwens, J. A. Hammerschmidt, M. M. Grzeskowiak, T. A. Stegink, P. M. Yorba, and W. F. Polik, "Pure vibrational spectroscopy of S0 formaldehyde by dispersed fluorescence," *Journal of Chemical Physics*, vol. 104, no. 2, pp. 460–479, 1996, ISSN: 00219606. DOI: 10.1063/1.470844.
- [92] K. A. Rahman, V. Athmanathan, M. N. Slipchenko, T. R. Meyer, and S. Roy, "Pressure-scaling characteristics of femtosecond two-photon laser-induced fluorescence of carbon monoxide.," *Applied Optics*, vol. 58, no. 27, pp. 7458–7465, 2019.
- [93] R. P. Lucht, "Three-laser coherent anti-Stokes Raman scattering measurements of two species," *Optics Letters*, vol. 12, no. 2, p. 78, 1987, ISSN: 0146-9592. DOI: 10. 1364/ol.12.000078.
- [94] S. Roy, T. R. Meyer, M. S. Brown, V. N. Velur, R. P. Lucht, and J. R. Gord, "Triplepump coherent anti-Stokes Raman scattering (CARS): Temperature and multiplespecies concentration measurements in reacting flows," *Optics Communications*, vol. 224, no. 1-3, pp. 131–137, 2003, ISSN: 00304018. DOI: 10.1016/S0030-4018(03)01688-2.
- [95] S. Roy, T. R. Meyer, R. P. Lucht, M. Afzelius, P.-E. Bengtsson, and J. R. Gord, "Dualpump dual-broadband coherent anti-Stokes Raman scattering in reacting flows," *Optics Letters*, vol. 29, no. 16, p. 1843, 2004, ISSN: 0146-9592. DOI: 10.1364/ol.29.001843.
- [96] S. Roy, T. R. Meyer, R. P. Lucht, V. M. Belovich, E. Corporan, and J. R. Gord, "Temperature and CO2 concentration measurements in the exhaust stream of a liquidfueled combustor using dual-pump coherent anti-Stokes Raman scattering (CARS) spectroscopy," *Combustion and Flame*, vol. 138, no. 3, pp. 273–284, 2004, ISSN: 00102180. DOI: 10.1016/j.combustflame.2004.04.012.
- [97] M. C. Weiki, T. Seeger, R. Hierold, and A. Leipertz, "Dual-pump CARS measurements of N2, H2 and CO in a partially premixed flame," *Journal of Raman Spec*troscopy, vol. 38, no. 8, pp. 983–988, 2007.
- [98] S. M. Green, P. J. Rubas, M. A. Paul, J. E. Peters, and R. P. Lucht, "Simultaneous Detection of Nitrogen and Methane," *Applied Optics*, 1998.

- [99] S. A. Tedder, P. M. Danehy, and A. D. Cutler, "Width-increased dual-pump enhanced coherent anti-Stokes Raman Spectroscopy (WIDECARS)," 27th AIAA Aerodynamic Measurement Technology and Ground Testing Conference 2010, vol. 1, no. 8, pp. 1305– 1313, 2010. DOI: 10.2514/6.2010-4807.
- [100] E. C. Gallo, L. M. Cantu, A. D. Cutler, C. P. Goyne, and J. C. McDaniel, "WIDE-CARS Measurements of a Premixed Ethylene-Air Flame in a Small-Scale Dual-Mode Scramjet Combustor," in AIAA Scitech 2016, 2016.
- [101] A. D. Cutler, E. C. Gallo, and L. M. Cantu, "WIDECARS spectra fitting in a premixed ethylene-air flame," *Journal of Raman Spectroscopy*, vol. 47, 2015.
- [102] M. D. Rahn, T. A. King, A. A. Gorman, and I. Hamblett, "Photostability enhancement of Pyrromethene 567 and Perylene Orange in oxygen-free liquid and solid dye lasers," *Applied Optics*, vol. 36, no. 24, p. 5862, 1997, ISSN: 0003-6935. DOI: 10.1364/ ao.36.005862.
- [103] S. P. Kearney and M. N. Jackson, "Dual-pump coherent anti-stokes Raman scattering thermometry in heavily sooting flames," *AIAA Journal*, vol. 45, no. 12, pp. 2947–2956, 2007, ISSN: 00011452. DOI: 10.2514/1.31054.
- [104] L. I. Liu, N. N. Barashkov, C. P. Palsule, S. Gangopadhyay, and W. L. Borst, "Intermolecular energy transfer in binary systems of dye polymers," *Journal of Applied Physics*, vol. 88, no. 8, pp. 4860–4870, 2000, ISSN: 00218979. DOI: 10.1063/1.1309037.
- [105] M. Álvarez, F. Amat-Guerri, A. Costela, I. García-Moreno, M. Liras, and R. Sastre, "Laser emission from mixtures of dipyrromethene dyes in liquid solution and in solid polymeric matrices," *Optics Communications*, vol. 267, no. 2, pp. 469–479, 2006, ISSN: 00304018. DOI: 10.1016/j.optcom.2006.06.059.
- [106] R. Palmer, "The CARSFTComputer Code for Calculating Coherent Anti-Stokes Raman Spectra: User and Programmer Information," Sandia National Laboratories, Tech. Rep., 1989.
- [107] G. Magnotti, A. D. Cutler, and P. M. Danehy, "Development of a dual-pump coherent anti-Stokes Raman spectroscopy system for measurements in supersonic combustion," *Applied Optics*, vol. 52, no. 20, pp. 4779–4791, 2013, ISSN: 15394522. DOI: 10.1364/ AO.52.004779.
- [108] G. Sutton, A. Levick, G. Edwards, and D. Greenhalgh, "A combustion temperature and species standard for the calibration of laser diagnostic techniques," *Combustion and Flame*, vol. 147, no. 1-2, pp. 39–48, 2006, ISSN: 00102180. DOI: 10.1016/j. combustflame.2006.07.013.

- [109] F. Vestin, M. Afzelius, C. Brackmann, and P. E. Bengtsson, "Dual-broadband rotational CARS thermometry in the product gas of hydrocarbon flames," *Proceedings of* the Combustion Institute, vol. 30, no. 1, pp. 1673–1680, 2005, ISSN: 15407489. DOI: 10.1016/j.proci.2004.08.043. [Online]. Available: http://dx.doi.org/10.1016/j.proci. 2004.08.043.
- [110] S. Prucker, W. Meier, and W. Stricker, "A flat flame burner as calibration source for combustion research: Temperatures and species concentrations of premixed H2/air flames," *Review of Scientific Instruments*, vol. 65, no. 9, pp. 2908–2911, 1994, ISSN: 00346748. DOI: 10.1063/1.1144637.
- [111] M. N. Slipchenko, T. R. Meyer, and S. Roy, "Advances in burst-mode laser diagnostics for reacting and nonreacting flows," *Proceedings of the Combustion Institute*, vol. 38, no. 1, pp. 1533–1560, 2021, ISSN: 15407489. DOI: 10.1016/j.proci.2020.07.024.
- [112] M. E. Smyser, E. L. Braun, V. Athmanathan, M. N. Slipchenko, S. Roy, and T. R. Meyer, "Dual-output fs/ps burst-mode laser for megahertz-rate rotational coherent anti-Stokes Raman scattering," *Optics Letters*, vol. 45, no. 21, p. 5933, 2020, ISSN: 0146-9592. DOI: 10.1364/ol.404984.
- [113] J. G. Mance, M. N. Slipchenko, and S. Roy, "Regenerative amplification and bifurcations in a burst-mode Nd:YAG laser," *Optics Letters*, vol. 40, no. 21, p. 5093, 2015, ISSN: 0146-9592. DOI: 10.1364/ol.40.005093.
- [114] J. D. Miller, M. Slipchenko, T. R. Meyer, N. Jiang, W. R. Lempert, and J. R. Gord, "Ultrahigh-frame-rate OH fluorescence imaging in turbulent flames using a burstmode optical parametric oscillator," *Optics Letters*, vol. 34, no. 9, p. 1309, 2009, ISSN: 0146-9592. DOI: 10.1364/ol.34.001309.
- [115] P. S. Hsu, M. N. Slipchenko, N. Jiang, C. A. Fugger, A. M. Webb, V. Athmanathan, T. R. Meyer, and S. Roy, "Megahertz-rate OH planar laser-induced fluorescence imaging in a rotating detonation combustor," *Optics Letters*, vol. 45, no. 20, p. 5776, 2020, ISSN: 0146-9592. DOI: 10.1364/ol.403199.
- [116] P. S. Hsu, N. Jiang, J. S. Jewell, J. J. Felver, M. Borg, R. Kimmel, and S. Roy, "100 kHz PLEET velocimetry in a Mach-6 Ludwieg tube," *Optics Express*, vol. 28, no. 15, pp. 21982–21992, 2020, ISSN: 1094-4087. DOI: 10.1364/OE.391302.
- [117] J. D. Miller, M. N. Slipchenko, J. G. Mance, S. Roy, and J. R. Gord, "1-kHz twodimensional coherent anti-Stokes Raman scattering (2D-CARS) for gas-phase thermometry," *Optics Express*, vol. 24, no. 22, p. 24971, Oct. 2016, ISSN: 1094-4087. DOI: 10.1364/oe.24.024971.

- [118] J. Felver, M. N. Slipchenko, E. L. Braun, T. R. Meyer, and S. Roy, "High-energy laser pulses for extended duration megahertz-rate flow diagnostics," *Optics Letters*, vol. 45, no. 16, p. 4583, 2020, ISSN: 0146-9592. DOI: 10.1364/ol.400831.
- [119] S. Roy, T. R. Meyer, and J. R. Gord, "Time-resolved dynamics of resonant and nonresonant broadband picosecond coherent anti-Stokes Raman scattering signals," *Applied Physics Letters*, vol. 87, no. 26, pp. 1–3, 2005, ISSN: 00036951. DOI: 10.1063/ 1.2159576.
- [120] C. J. Kliewer, Y. Gao, T. Seeger, J. Kiefer, B. D. Patterson, and T. B. Settersten, "Picosecond time-resolved pure-rotational coherent anti-Stokes Raman spectroscopy in sooting flames," *Proceedings of the Combustion Institute*, 2011, ISSN: 15407489. DOI: 10.1016/j.proci.2010.05.067.
- [121] S. Roy, P. S. Hsu, N. Jiang, M. N. Slipchenko, and J. R. Gord, "100-kHz-rate gasphase thermometry using 100-ps pulses from a burst-mode laser," *Optics Letters*, vol. 40, no. 21, p. 5125, 2015, ISSN: 0146-9592. DOI: 10.1364/ol.40.005125.
- [122] T. Nobuyuki, Y. Hidehiro, A. Takao, and F. Akira, "High-Fidelity Teleportation beyond the No-Cloning Limit and Entanglement Swapping for Continuous Variables," *Physical Review Letters*, vol. 94, no. 22, 2005.
- [123] Y. Fu, K. Midorikawa, and E. J. Takahashi, "Towards a petawatt-class few-cycle infrared laser system via dual-chirped optical parametric amplification," *Scientific Reports*, vol. 8, no. 1, pp. 1–11, 2018, ISSN: 20452322. DOI: 10.1038/s41598-018-25783-0. [Online]. Available: http://dx.doi.org/10.1038/s41598-018-25783-0.
- [124] A. Vedadi, A. M. Ariaei, M. M. Jadidi, and J. A. Salehi, "Theoretical study of high repetition rate short pulse generation with fiber optical parametric amplification," *Journal of Lightwave Technology*, vol. 30, no. 9, pp. 1263–1268, 2012, ISSN: 07338724. DOI: 10.1109/JLT.2012.2184262.
- [125] A. You, M. A. Y. Be, and I. In, "harmonic generation and optical parametric amplification in a lithium triborate crystal," vol. 1579, no. 1991, 1998.
- [126] Z. Sun, M. Ghotbi, and M. E. Zadeh, "Widely tunable picosecond optical parametric generation and amplification in BiB3O6," *Optics Express*, vol. 15, no. 7, p. 4139, 2007, ISSN: 1094-4087. DOI: 10.1364/oe.15.004139.
- [127] D. Pang, R. Zhang, J. Sun, and Q. Wang, "Theoretical analysis of noncollinear phasematched optical parametric generation in BBO crystal," *Optics and Laser Technology*, vol. 33, no. 4, pp. 249–254, 2001, ISSN: 00303992. DOI: 10.1016/S0030-3992(01)00033-0.

- [128] L. Carrion and J.-P. Girardeau-Montaut, "Development of a simple model for optical parametric generation," *Journal of the Optical Society of America B*, vol. 17, no. 1, p. 78, 2000, ISSN: 0740-3224. DOI: 10.1364/josab.17.000078.
- [129] J. Fan, W. Chen, C. Gu, J. Zhao, Y. Song, L. Chai, C. Wang, and M. Hu, "Noise characteristics of fiber-laser pumped femtosecond optical parametric generation," 2017 Conference on Lasers and Electro-Optics, CLEO 2017 - Proceedings, vol. 2017-Janua, no. 20, pp. 1–2, 2017. DOI: 10.1364/CLEO{\ }AT.2017.JTh2A.83.
- [130] C. Manzoni and G. Cerullo, "Design criteria for ultrafast optical parametric amplifiers," *Journal of Optics (United Kingdom)*, vol. 18, no. 10, 2016, ISSN: 20408986. DOI: 10.1088/2040-8978/18/10/103501.
- [131] R. A. Baumgartner, R. Byer, and A. S. O. N. Interactions, "Optical Parametric Amplification," *Quantum*, no. 6, pp. 432–444, 1979, ISSN: 0169409X. DOI: 10.1016/j. addr.2004.03.001.
- [132] J. Y. Zhang, J. Y. Huang, Y. R. Shen, and C. Chen, "Optical parametric generation and amplification in barium borate and lithium triborate crystals," *Journal of the Optical Society of America B*, vol. 10, no. 9, p. 1758, 1993, ISSN: 0740-3224. DOI: 10.1364/josab.10.001758.
- [133] J. D. Miller, "Hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering for gas-phase temperature measurements," 2012.
- [134] J. W. Tröger, C. Meißner, and T. Seeger, "High temperature O2 vibrational CARS thermometry applied to a turbulent oxy-fuel combustion process," *Journal of Raman Spectroscopy*, vol. 47, no. 9, pp. 1149–1156, 2016, ISSN: 10974555. DOI: 10.1002/jrs. 4937.
- [135] A. Montello, Z. Yin, D. Burnette, I. V. Adamovich, and W. R. Lempert, "Picosecond CARS measurements of nitrogen vibrational loading and rotational/translational temperature in non-equilibrium discharges," *Journal of Physics D: Applied Physics*, vol. 46, no. 46, 2013, ISSN: 00223727. DOI: 10.1088/0022-3727/46/46/464002.
- [136] J. D. Miller, M. N. Slipchenko, T. R. Meyer, H. U. Stauffer, and J. R. Gord, "Hybrid femtosecond / picosecond coherent anti-Stokes Raman scattering for high-speed gasphase thermometry," vol. 35, no. 14, pp. 2430–2432, 2010.
- [137] K. A. Rahman, E. L. Braun, M. N. Slipchenko, S. Roy, and T. R. Meyer, "Flexible chirp-free probe pulse amplification for kHz fs/ps rotational CARS," *Optics Letters*, vol. 45, no. 2, p. 503, 2020, ISSN: 0146-9592. DOI: 10.1364/ol.382033.

- [138] C. N. Dennis, A. Satija, and R. P. Lucht, "High dynamic range thermometry at 5 kHz in hydrogen-air diffusion flame using chirped-probe-pulse femtosecond coherent antistokes Raman scattering," *Journal of Raman Spectroscopy*, vol. 47, no. 2, pp. 177– 188, Feb. 2016, ISSN: 03770486. DOI: 10.1002/jrs.4773. [Online]. Available: https: //onlinelibrary.wiley.com/doi/10.1002/jrs.4773.
- [139] A. Bohlin, B. D. Patterson, and C. J. Kliewer, "Communication: Simplified two-beam rotational CARS signal generation demonstrated in 1D," *Journal of Chemical Physics*, vol. 138, no. 8, 2013, ISSN: 00219606. DOI: 10.1063/1.4793556.
- [140] H. Zhao, Z. Tian, T. Wu, Y. Li, and H. Wei, "Sensitive hybrid femtosecond/picosecond vibrational coherent anti-Stokes Raman scattering thermometry using optimized probe time delays," *Applied Physics Letters*, vol. 116, no. 11, 2020, ISSN: 00036951. DOI: 10.1063/1.5140212.
- [141] M. Scherman, M. Nafa, T. Schmid, A. Godard, A. Bresson, B. Attal-Tretout, and P. Joubert, "Rovibrational hybrid fs/ps CARS using a volume Bragg grating for N_2 thermometry," *Optics Letters*, vol. 41, no. 3, p. 488, 2016, ISSN: 0146-9592. DOI: 10.1364/ol.41.000488.
- [142] E. H. Van Veen and D. Roekaerts, "Thermometry for turbulent flames by coherent anti-Stokes Raman spectroscopy with simultaneous referencing to the modeless excitation profile," *Applied Optics*, vol. 44, no. 32, pp. 6995–7004, 2005, ISSN: 15394522. DOI: 10.1364/AO.44.006995.
- [143] F. Grisch, P. Bouchardy, and W. Clauss, "CARS thermometry in high pressure rocket combustors," *Aerospace Science and Technology*, vol. 7, no. 4, pp. 317–330, 2003, ISSN: 12709638. DOI: 10.1016/S1270-9638(03)00017-8.
- [144] Y. Guan, J. W. Haus, and P. Powers, "Macroscopic quantum fluctuations of pulsed nanosecond optical parametric generation in periodically-poled LiNb O3," *Physical Review A - Atomic, Molecular, and Optical Physics*, vol. 71, no. 2, pp. 1–9, 2005, ISSN: 10941622. DOI: 10.1103/PhysRevA.71.023809.
- [145] S. P. Kearney, "Bandwidth optimization of femtosecond pure-rotational coherent anti-Stokes Raman scattering by pump/Stokes spectral focusing," *Applied Optics*, vol. 53, no. 28, p. 6579, 2014, ISSN: 0003-6935. DOI: 10.1364/ao.53.006579.
- [146] F. Mazza, L. Castellanos, D. Kliukin, and A. Bohlin, "Coherent Raman imaging thermometry with in-situ referencing of the impulsive excitation efficiency," *Proceedings* of the Combustion Institute, vol. 38, no. 1, pp. 1895–1904, 2021, ISSN: 15407489. DOI: 10.1016/j.proci.2020.06.360.

- [147] H. Wang, G. Jian, W. Zhou, J. B. DeLisio, V. T. Lee, and M. R. Zachariah, "Metal Iodate-Based Energetic Composites and Their Combustion and Biocidal Performance," ACS Applied Materials and Interfaces, vol. 7, no. 31, pp. 17363–17370, 2015, ISSN: 19448252. DOI: 10.1021/acsami.5b04589.
- [148] R. Ames and M. Murphy, "Diagnostic techniques for multiphase blast fields," in 24th International Symposium on Ballistics, New Orleans, LA, September, 2008, pp. 22– 26. [Online]. Available: https://scholar.google.com/scholar?hl=en&as_sdt=0% 2C5&q=R.+Ames%2C+M.+Murphy%2C+diagnostic+techniques&btnG=&oq=R. +Ames%2C+M.+Murphy%2C+diagnostic+techni.
- [149] A. R. Kiwan, "An Overview of High-Explosive (HE) Blast Damage Mechanisms and Vulnerability Prediction Methods," Defense Technical information center, Tech. Rep., Aug. 1997. [Online]. Available: https://apps.dtic.mil/sti/citations/ADA329188.
- [150] A. D. Brown, "High Speed Laser Diagnostics for bioagent defeat applications," PhD thesis, Purdue University, 2019.
- [151] G. C. Mathews and C. S. Goldenstein, "Wavelength-Modulation-Spectroscopy Diagnostics for Characterizing Metallized and Halogenated Fireballs of Energetic Materials," in AIAA Scitech 2020 Forum, Reston, Virginia: American Institute of Aeronautics and Astronautics, Jan. 2020, ISBN: 978-1-62410-595-1. DOI: 10.2514/6.2020-0301. [Online]. Available: https://arc.aiaa.org/doi/10.2514/6.2020-0301.
- [152] P. S. Hsu, N. Jiang, D. Lauriola, S. W. Grib, S. A. Schumaker, A. W. Caswell, and S. Roy, "10 kHz 2D thermometry in turbulent reacting flows using two-color OH planar laser-induced fluorescence," *Applied Optics*, vol. 60, no. 15, p. C1, 2021, ISSN: 1559-128X. DOI: 10.1364/ao.419330.
- [153] P. S. Hsu, N. Jiang, J. J. Felver, D. K. Lauriola, P. M. Danehy, and S. Roy, "10 kHz two-color OH PLIF thermometry using a single burst-mode OPO," *Optics Letters*, vol. 46, no. 10, p. 2308, 2021, ISSN: 0146-9592. DOI: 10.1364/ol.423062.
- [154] S. Roy, N. Jiang, H. U. Stauffer, J. B. Schmidt, W. D. Kulatilaka, T. R. Meyer, C. E. Bunker, and J. R. Gord, "Spatially and temporally resolved temperature and shock-speed measurements behind a laser-induced blast wave of energetic nanoparticles," *Journal of Applied Physics*, vol. 113, no. 18, 2013, ISSN: 00218979. DOI: 10.1063/1. 4804410.

- Y. Chen, D. R. Guildenbecher, K. N. Hoffmeister, M. A. Cooper, H. L. Stauffacher, M. S. Oliver, and E. B. Washburn, "Study of aluminum particle combustion in solid propellant plumes using digital in-line holography and imaging pyrometry," *Combustion and Flame*, vol. 182, pp. 225–237, 2017, ISSN: 15562921. DOI: 10.1016/j. combustflame.2017.04.016. [Online]. Available: http://dx.doi.org/10.1016/j. combustflame.2017.04.016.
- [156] A. Illarianov and R. Syunyaev, "Comptonization, characteristic radiation spectra, and thermal balance of low-density plasma," *Soviet Astronomy*, vol. 18, no. 4, pp. 413– 419, 1975.
- [157] C. E. Dedic, T. R. Meyer, and J. B. Michael, "Single-shot ultrafast coherent anti-Stokes Raman scattering of vibrational/rotational nonequilibrium," *Optica*, vol. 4, no. 5, p. 563, 2017, ISSN: 2334-2536. DOI: 10.1364/optica.4.000563.
- [158] M. A. Woodmansee, V. Iyer, J. C. Dutton, and R. P. Lucht, "Nonintrusive pressure and temperature measurements in an underexpanded sonic jet flowfield," AIAA Journal, vol. 42, no. 6, pp. 1170–1180, 2004, ISSN: 00011452. DOI: 10.2514/1.10418.
- [159] R. D. Hancock, F. R. Schauer, R. P. Lucht, and R. L. Farrow, "Dual-pump coherent anti-Stokes Raman scattering measurements of nitrogen and oxygen in a laminar jet diffusion flame," *Applied Optics*, vol. 36, no. 15, p. 3217, 1997, ISSN: 0003-6935. DOI: 10.1364/ao.36.003217.
- [160] A. Bohlin, E. Nordström, H. Carlsson, X. S. Bai, and P. E. Bengtsson, "Pure rotational CARS measurements of temperature and relative O 2-concentration in a low swirl turbulent premixed flame," *Proceedings of the Combustion Institute*, vol. 34, no. 2, pp. 3629–3636, 2013, ISSN: 15407489. DOI: 10.1016/j.proci.2012.05.016.
- [161] J. Barros, M. Scherman, E. Lin, N. Fdida, R. Santagata, B. Attal-Tretout, and A. Bresson, "5 kHz single shot hybrid fs/ps-CARS thermometry in an atmospheric flame," *Optics Express*, vol. 28, no. 23, p. 34656, 2020, ISSN: 1094-4087. DOI: 10. 1364/oe.404380.
- [162] K. P. Lynch and J. L. Wagner, "A free-piston driven shock tube for generating extreme aerodynamic environments," in *AIAA Scitech 2019 Forum*, 2019.
- [163] S. Roy, J. D. Miller, M. N. Slipchenko, P. S. Hsu, J. G. Mance, T. R. Meyer, and J. R. Gord, "100-ps-pulse-duration, 100-J burst-mode laser for kHz–MHz flow diagnostics," vol. 39, no. 22, pp. 6462–6465, 2014.

- [164] T. Seeger and A. Leipertz, "Experimental comparison of single-shot broadband vibrational and dual-broadband pure rotational coherent anti-Stokes Raman scattering in hot air," *Applied Optics*, vol. 35, no. 15, p. 2665, 1996, ISSN: 0003-6935. DOI: 10.1364/ao.35.002665.
- [165] D. R. Snelling, G. J. Smallwood, R. A. Sawchuk, and T. Parameswaran, "Precision of multiplex CARS temperatures using both single-mode and multimode pump lasers," *Applied Optics*, vol. 26, no. 1, p. 99, 1987, ISSN: 0003-6935. DOI: 10.1364/ao.26.000099.
- S. P. Kearney, "Hybrid fs/ps rotational CARS temperature and oxygen measurements in the product gases of canonical flat flames," *Combustion and Flame*, vol. 162, no. 5, pp. 1748–1758, 2014, ISSN: 15562921. DOI: 10.1016/j.combustflame.2014.11.036.
 [Online]. Available: http://dx.doi.org/10.1016/j.combustflame.2014.11.036.
- [167] D. R. Richardson, R. P. Lucht, W. D. Kulatilaka, S. Roy, and J. R. Gord, "Theoretical modeling of single-laser-shot, chirped-probe-pulse femtosecond coherent anti-Stokes Raman scattering thermometry," *Applied Physics B: Lasers and Optics*, vol. 104, no. 3, pp. 699–714, 2011, ISSN: 09462171. DOI: 10.1007/s00340-011-4489-0.
- [168] R. P. Lucht, P. J. Kinnius, S. Roy, and J. R. Gord, "Theory of femtosecond coherent anti-Stokes Raman scattering spectroscopy of gas-phase transitions," *Journal of Chemical Physics*, vol. 127, no. 4, 2007, ISSN: 00219606. DOI: 10.1063/1.2751184.
- [169] E. Jans, S. P. Kearney, D. J. Armstrong, and A. V. Smith, "Demonstration of a burst-mode-pumped noncolinear optical parametric oscillator (NOPO) for broadband CARS diagnostics in gases," in AIAA Scitech 2022 Forum, 2022.
- [170] D. Herrmann, L. Veisz, R. Tautz, A. Buck, F. Tavella, K. Schmid, V. Pervak, M. Scharrer, P. Russell, and F. Krausz, "Generation of three-cycle, 16 tw light pulses by use of optical parametric chirped pulse amplification," *Optics InfoBase Conference Papers*, vol. 34, no. 16, pp. 2459–2461, 2009, ISSN: 21622701.
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PUBLICATIONS

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- Lauriola D. K. Hsu, P.S., Jiang, N., Slipchenko, M.N., Meyer, T.R., Roy, S., Burst-mode 100 kHz N2 ps-CARS flame thermometry with concurrent nonresonant background referencing, Optics Letters, 46 (21),2021, 5489-5492
- Lauriola D.K., Brown, A.D. Hsu, P., Jiang, N., Roy, S., Meyer T.R., Son, S.F., 100 kHz burst-mode picosecond vibrational N₂ CARS thermometry in energetic combustion environments, AIAA Scitech 2022 Forum, 1943,2022
- Hsu, P.S., Lauriola, D.K., Frueh, S., Chen, X., Cinibulk, M. Roy. S., (2021). Compact fiber-coupled UV-NIR hyperspectral imaging sensor for characterizing ultra-high temperature ceramic materials, Applied optics, 60(15),.
- Hsu, P.S., Jiang, N., Lauriola, D.K., Grib S.W., Schumaker S.A., Caswell, A.W., Roy, S. (2021), 10 kHz 2D thermometry in turbulent reacting flows using two-color OH planar laserinduced fluorescence, Applied optics, 60(15)
- Hsu,P.S., Jiang, N., Felver, J.J., Lauriola, D.K., Danehy, P.M., Roy,S., 10 kHz two-color OH PLIF thermometry using a single burst-mode OPO, Optics Letters, 46 (10),2308-2311,2021
- Athmanathan, V., K. A. Rahman, Lauriola, D.K., J. Braun, G. Paniagua, M. N. Slipchenko, S. Roy, and T. R. Meyer, "Femtosecond/picosecond rotational coherent anti-Stokes Raman scattering thermometry in the exhaust of a rotating detonation combustor," Combust. Flame (2021).
- Fisher, J.M., Brown, A. D., Lauriola, D.K., Slipchenko, M.N., Meyer, T.R. (2020), Femtosecond laser activation and sensing of hydroxyl for velocimetry in reacting flows, Applied Optics, 59(34) ,10853-10861

- Rock, N., Hsu, P.S., Lauriola, D.K., Rahman, N., Estevadeordal, J., Grib, S.W., Jiang, N. Kearney, S.P., Wrezinski, P., (2020) WIDECARS multi-parameter measurements in premixed ethylene–air flames using a wavelength stable ultrabroadband dye laser, Applied Optics, 59 (8) 2649-2655.
- Hsu, P.S., Lauriola, D.K., Jiang, N., Miller J.D., Gord, J.R., Roy, S.R. (2017), Fibercoupled, UV–SWIR hyperspectral imaging sensor for combustion diagnostics Applied Optics 56 (21) 6029-6034
- Lauriola, D.K., Gomez, M. Meyer, T.R., Son, S.F. Slipchenko, M., Roy, S (2019). High speed particle image velocimetry and particle tracking methods in reactive and nonreactive flows, AIAA Scitech 2019 Forum.
- Lauriola, D.K., Meyer, T.R., Gomez, M., Roy,S, Slipchenko,M.N., Gord, J.R., Son S.F., (2018). KHz–MHz Rate Laser-Based Tracking of Particles and Product Gases for Multiphase Blast Fields, IEEE Research and Applications of Photonics in Defense Conference (RAPID)
- Kearney S.P., Daniel, K., Wagner, J.L., Lynch, K.P., Downing, C.R., Lauriola D.K., Leicht, J., Slipchenko, M., Burst-Mode Coherent Anti-Stokes Raman Scattering N₂ Thermometry in the Sandia Free-Piston Shock Tube, AIAA Scitech 2022 Forum, 0894,2022
- Jiang, N., Hsu, P.,Slipchenko, M., Roy, S., Lauriola D.K.,Webb A.M., MHz rate Flow Diagnostics in CUBRC Mach 10 Shock Tunnel, AIAA Scitech 2022 Forum, 1655,2022
- Hsu, P.Jiang, N., Lauriola D.K., Roy, S., Danehy, P.M., 10-kHz PLIF Thermometry for High-speed Jet Flame using Single Burst-mode OPO, AIAA Scitech 2022 Forum, 1523,2022
- Hsu, P.Jiang, N.,Lauriola D.K.,Leicht, J., Roy,S., Clifford, C., Braker, J.W.Pimmons,D.,Wehrmeyer, J.,Mach 4 Flow Velocimetry with 100-kHz PLEET and PIV in AEDC/AFRL Tunnel D, AIAA Scitech 2022 Forum, 0425,2022

17. Patnaik, A.K., Lauriola, D.K., Braun, E.L., Hsu, P.S., Meyer, T. R., Roy, S., (2020) High-Pressure Femtosecond Laser Induced Plasma Spectroscopy (FLIPS) for Combustion Diagnostics, Laser Applications to Chemical Security and Environmental Analysis (LACSEA)