Recent advances in ultrafast-laser-based spectroscopy and imaging for reacting plasmas and flames

Anil K Patnaik1,2, Igor Adamovich3, James R Gord4 and Sukesh Roy1,5

1 Spectral Energies, LLC, 4065 Executive Dr, Dayton, OH 45430, United States of America
2 Department of Physics, Wright State University, Dayton, OH 45435, United States of America
3 Department of Mechanical and Aerospace Engineering, Ohio State University, Columbus, OH 43210, United States of America
4 Air Force Research Laboratory, Aerospace Systems Directorate, WPAFB, OH 45433, United States of America

E-mail: sukesh.roy@spectralenergies.com

Received 19 July 2016, revised 10 July 2017
Accepted for publication 10 August 2017
Published 25 September 2017

Abstract
Reacting flows and plasmas are prevalent in a wide array of systems involving defense, commercial, space, energy, medical, and consumer products. Understanding the complex physical and chemical processes involving reacting flows and plasmas requires measurements of key parameters, such as temperature, pressure, electric field, velocity, and number densities of chemical species. Time-resolved measurements of key chemical species and temperature are required to determine kinetics related to the chemical reactions and transient phenomena. Laser-based, noninvasive linear and nonlinear spectroscopic approaches have proved to be very valuable in providing key insights into the physico-chemical processes governing reacting flows and plasmas as well as validating numerical models. The advent of kilohertz rate amplified femtosecond lasers has expanded the multidimensional imaging of key atomic species such as H, O, and N in a significant way, providing unprecedented insight into preferential diffusion and production of these species under chemical reactions or electric-field driven processes. These lasers not only provide 2D imaging of chemical species but have the ability to perform measurements free of various interferences. Moreover, these lasers allow 1D and 2D temperature-field measurements, which were quite unimaginable only a few years ago. The rapid growth of the ultrafast-laser-based spectroscopic measurements has been fueled by the need to achieve the following when measurements are performed in reacting flows and plasmas. They are: (1) interference-free measurements (collision broadening, photolytic dissociation, Stark broadening, etc), (2) time-resolved single-shot measurements at a rate of 1–10 kHz, (3) spatially-resolved measurements, (4) higher dimensionality (line, planar, or volumetric), and (5) simultaneous detection of multiple species. The overarching goal of this article is to review the current state-of-the-art ultrafast-laser-based spectroscopic techniques and their remarkable development in the past two decades in meeting one or all of the above five goals for the spectroscopic measurement of temperature, number density of the atomic and molecular species, and electric field.

Keywords: ultrafast, plasma, multiphoton imaging, CARS spectroscopy, TALIF

5 Author to whom any correspondence should be addressed.
1. Introduction

Research and development in reacting plasmas and flames is diverse and interdisciplinary [1–3]. Over the past decades, the continuously evolving field of plasmas has taken a number of leaps forward in the development of many new plasma technologies associated with defense, commercial, space, energy, medical, and consumer products. The parameter space of these plasmas ranges from low pressure (millibars) and low temperature [4] to extremely high pressure (up to gigabars) and high temperature (up to millions of K) [5]. The complex reacting plasma and flow environments involve a number of parameters that depend on their applications, which range from plasma-assisted combustion [6] to materials processing [7] to biomedical applications [8] to plasma reactors in fusion [5]. To characterize and understand the underlying physics and chemistry of these plasmas, it is vital to measure directly key performance parameters such as temperature, pressure, velocity, number densities of reacting species, and electric field. Laser-based, noninvasive, linear and nonlinear spectroscopic methods have proved to be valuable in providing insight into key physico-chemical processes that govern reacting plasmas. The limited spatial and temporal resolution of the conventional diagnostics technologies has prevented complete understanding of the plasma interactions [2], thereby limiting innovation and complicating product modification of plasma-based systems [9]. Plasma sources used for various applications are discussed below.

1.1. Brief discussion of plasma sources for various applications

Over the past two decades, extensive experimental and kinetic-modeling studies have been conducted in nonequilibrium plasmas over a wide range of experimental conditions [2, 10]. These efforts were prompted by a variety of potential applications such as plasma-flow control [11–13], plasma-assisted combustion [6, 14, 15], plasma-induced liquid-phase chemistry [16, 17], and plasma medicine [8, 18, 19]. The range of nonequilibrium plasma sources used for these applications is remarkably wide and includes numerous configurations of volumetric and surface dielectric-barrier discharges sustained by AC waveforms and short (nanosecond (ns)-duration) pulses, atmospheric-pressure plasma jets sustained by DC, AC, RF, and microwave waveforms, and arrays of microplasmas generated by microhollow-cathode DC discharges [20], to name a few. A detailed overview of these plasma sources can be found elsewhere (e.g. see [2, 6, 8, 11–19] and references therein) and is outside the scope of the present work. The focus of the present review is mainly on highly-transient plasmas such as those generated in streamers (see figures 1 and 2) [21, 22], high-peak-voltage ns-pulse-duration discharges (both volumetric and surface, see figures 3 and 4) [23, 24], and atmospheric-pressure plasma jets and plasma bullets (see figure 5) [25]. These discharges are known to exhibit highly complex behavior on short timescales. Recent advances in both experiments and kinetic modeling in this rapidly developing field can be found in a special issue on fast-pulsed discharges (see [26] and references therein).

One of the difficulties in understanding the kinetics of these plasmas is the lack of noninvasive, spatio-temporally resolved measurements for their characterization. To begin with, rapidly varying distribution of the electric field in these plasmas controls the electron-energy distribution function (EEDF) and energy partition among the internal energy modes of atoms and molecules during electron-impact processes. At these highly-transient conditions and in the presence of strong spatial gradients (such as in streamer-dominated plasmas), the EEDF may also be nonlocal, which significantly complicates the plasma kinetics. These dominant effects control the number densities of a variety of excited species and radicals, the kinetics of molecular-energy transfer, and the energy-thermalization rate. Quantitative insight into these processes requires spatio-temporally resolved measurements of density and temperature of electron, electric field, gas temperature, and species number densities in the plasma using nonintrusive, in situ experimental techniques.

The next subsection introduces the current state-of-the-art diagnostics and the diagnostic needs for reacting plasmas and flows.
1.2. Diagnostic needs for reacting plasmas and flames

For most of the plasmas discussed above, only a very small fraction of the neutral species at the target volume are ionized (see figure 6 in [2]), except for extreme conditions encountered in nuclear-fusion reactors [5]. Hence, in most cases the dominant species in the plasmas are neutral atoms and molecules, including vibrationally and electronically excited species and highly reactive radicals. Depending on specific energy loading, mixture composition, temperature, pressure, flow conditions, the electron-impact process, as well as energy transfer among excited species results in a wide range of plasma-chemical reactions. A common interest is shared in the research and development of many plasma applications to understand the spatial distribution and temporal evolution of key intermediate plasma species, including electrons, ions, metastable excited species, and highly reactive atoms and radicals [10]. Many of the excited species generated by electron impact and molecular collisions within the plasma decay spontaneously to emit radiation. Hence, the passive detection of the emitted light by optical emission spectroscopy is the simplest form of plasma diagnostics. However, this technique does not provide quantitative data unless the excitation and de-excitation mechanisms of the plasma are known exactly, such as those in well-calibrated equilibrium plasmas and flows [27]. However, most of the recent applications discussed in the earlier section are highly-transient and nonequilibrium in nature with rapidly changing reacting intermediates, chemical products, and their chemical kinetics. It is particularly important to quantify concentrations of the intermediates such as atomic neutrals, e.g. hydrogen, oxygen, nitrogen, and carbon. These intermediates are highly reactive and can be generated in significant concentrations to affect the macroscopic plasma conditions. Thus, absolute concentration measurements of important intermediate plasma species in nonequilibrium plasmas provide valuable insight that aids the understanding of the physical and chemical nature of these plasma systems and facilitates the development of model-based predictive capabilities.
In the review article entitled ‘The 2012 Plasma Roadmap’, Czarnetzki explicitly outlined the limitations in the current plasma-characterization capabilities and described the need for diagnostics and model development for different types of plasmas [2]. For quantifying the intermediates in reacting plasma and flow species, ideal diagnostic techniques should be nonintrusive, *in situ*, and species-selective, with a large dynamic range to permit the detection of short-lived reactive species with low densities, while avoiding saturation effects at higher densities. Conventional continuous-wave diode-laser-and ns-pulsed-laser-based spectroscopic techniques exhibit fundamental limitations, despite their ability to provide nonintrusive, *in situ*, and species-selective measurement platforms. For example, line-of-sight absorption-spectroscopy techniques often lack sufficient spatial resolution. Laser-induced fluorescence (LIF) is generally based on single-photon absorption and offers high spatial resolution. However, because of relatively strong absorption cross-sections, large concentrations can prove to be optically thick, resulting in significant probe-beam attenuation or stimulated-emission (SE) effects [28]. In addition, many key intermediates such as atomic hydrogen, oxygen, and nitrogen have a large energy spacing between the ground and excited electronic states. Such large energy gaps require high single-photon energies with wavelengths in the vacuum-ultraviolet (VUV) region, which are relatively difficult to generate and pose significant problems for propagation through air. Furthermore, the laser-based, linear optical techniques such as laser-induced emission and absorption in plasmas and flows require extensive dependence on models for complex-flow characterization; still, such techniques yield only limited spatial and temporal resolution [10, 29]. Most state-of-the-art plasma diagnostics are limited to emission or line-of-sight absorption spectroscopy, which yields mainly qualitative information or time-averaged and spatially-averaged quantitative information that is suitable for equilibrium plasmas only [30]. Employing calibration techniques such as Rayleigh scattering with inert gases or with LIF of a mixture with known concentration of the target molecule and extensive modeling of the collisional processes, spatially-resolved absolute concentration measurements of radical species such as OH and NO employing LIF- and planar-LIF (PLIF) have been demonstrated in different plasma conditions [31–35]. However, ns-laser-based LIF is still limited to lower plasma densities, because of strong single-photon resonant absorptions [27].

In nonequilibrium reacting plasmas, the rapidly evolving physical and chemical processes that involve many reacting intermediate species, such as O, N, and H, strongly influence the outcome of the plasma process [10]. To address the above-mentioned limitations with linear optical methods, multiphoton excitation has been developed and employed. Multiphoton approaches offer two significant advantages: (1) red-shifted wavelengths (away from the VUV wavelengths) allow beam propagation with minimal absorption in air, and (2) smaller absorption cross-sections permit high-resolution reacting-species measurements at higher concentrations. Two-photon-absorption LIF (TALIF) was first demonstrated for atomic hydrogen and deuterium by Bokor *et al* [36] and has since been dramatically expanded to the detection of many ground-state atomic species. Traditionally, ns-laser systems have been employed to probe TALIF transitions utilizing numerous excitation schemes. However, the relatively high fluence of typical ns-laser pulses that are used to overcome the relatively small multiphoton-absorption cross-sections can result in significant interference from photodissociation and photoionization within the medium, resulting in substantial photolytic interference of the TALIF signal. For example, photodissociation of O2 could create an O atom, which would interfere with the chemically produced O atom in the TALIF-based concentration measurement [27]. Similar interference is also prevalent in reacting flames where methyl (CH3) and water (H2O) can photodissociate to produce an H or O atom and, hence, create significant interference during the probing processes [37–40]. A partial suppression of this photolytic interference was reported for H- and O-atom TALIF schemes using ps-duration pump pulses [41], emphasizing the potential of ultrafast-pulse excitation in reducing or removing photolytic interferences during the measurement of atomic or molecular species via TALIF. The advantage of moving towards a shorter pulse is that higher irradiance can be realized with orders-of-magnitude lower fluence to achieve a similar level of signal-to-noise ratio (SNR) and, therefore, interference-free single-shot imaging capabilities can be extended to higher dimensions. Section 3 contains a detailed discussion of how ultrafast-laser-based interference-free TALIF detection has significantly expanded measurement capabilities.

Furthermore, a variety of promising nonlinear optical techniques, such as four-wave mixing (FWM) and coherent anti-Stokes Raman scattering (CARS), have been developed in the past four decades and extensively used for thermometric studies in nonequilibrium plasmas [42] and flow diagnostics [28]. Such FWM techniques generally provide higher spectral and spatial selectivity than the linear spectroscopic techniques. However, most of those efforts were carried out through the use of ns-duration laser pulses [43]. Typically, ns-laser-based CARS causes an array of signal interferences and other limitations such as: (a) contribution from nonresonant background (NRB) that limits the accuracy and degrades the sensitivity of the technique, (b) dependence of the signal on the collisional environment via collisional dephasing, where measurements are strongly dependent on the accuracy of the collisional models, (c) inability to respond to the dynamical changes of temperature and number densities of reacting species in highly-transient reacting plasmas and flows, because of the low repetition rate of the laser, and (d) insufficient intensity to perform measurements along a line or in a plane. During the past decade, it has been demonstrated that ultrafast-laser-based CARS has the potential to overcome the shortcomings generally encountered with ns-CARS [3], which is discussed in detail in section 4.

Remarkable advancements in kilohertz-rate amplified femtosecond (fs) lasers and ultrafast nonlinear optical techniques have significantly expanded the diagnostics capability for reacting plasmas and flames [3]. Employing fs-laser-based TALIF, photolytic-interference-free multidimensional imaging of the key reacting species H, O, N, OH, and CO has been demonstrated, providing unprecedented insight into the
production and preferential diffusion of these species in electrically- or chemically-driven processes \[44, 45\]; fs-TALIF is described in detail in section 3. In addition, high-power ultrafast lasers have enabled NRB-free, single-shot, multi-dimensional temperature measurements at higher than kHz repetition rates, which was quite unimaginable only a few years ago (see section 4). The intense growth in ultrafast-laser-based spectroscopy during the past decade has been driven by the following goals: (1) interference-free measurement, (2) time-resolved single-shot measurement for dynamic environments, (3) spatially-resolved measurement, (4) increased dimensionality, and (5) measurement of multiple species simultaneously. Throughout this article, the paths followed to reach each of the above goals of ultrafast-diagnostics development for reacting plasmas and flows will be discussed.

1.3. Background physics of the effect of laser duration on laser-plasma interactions

Laser-based diagnostics of plasma relies on the interaction of the laser with ions, electrons, molecules, and atomic species at the target volume of the plasma. The specific approach depends on the species under consideration, environmental conditions (temperature, pressure, neighboring species), and laser parameters (laser energy, pulse duration, and bandwidth). While the impact of the laser parameters and other environmental conditions will be discussed throughout this review, in the following we present a brief overview of various laser parameters of interest related to a range of pulse durations.

The laser parameter that is often used to quantify LIF and PLIF excitation is laser fluence \( F \), which is defined as time-integrated photon flux or laser energy \( \varepsilon \) delivered per unit area \( A \); i.e. \( F = \varepsilon / A \) and typically expressed in terms of \( \text{J cm}^{-2} \). Typically, LIF/PLIF signal scales with the fluence in the linear regime (i.e. below saturation). However, with ps and fs excitations, the fluence-based description fails to explain the laser-plasma interaction, because of the absence of the pulse duration in the underlying formulation. In the short-pulse regime, the underlying physics is governed by the proximity of the laser timescales with respect to the collisional timescales.

Furthermore, laser pulse with electric field \( \vec{E}(t) \) coherently interact with the plasma species with dipole moments \( \langle d_i \rangle \) that determine the Rabi frequency \( \Omega_i(t) = \langle d_i \rangle \cdot \vec{E}(t) / \hbar \) that defines the rate at which the coherent population transfer takes place within the plasma species at a given instant \( t \); here, \( \hbar = h / 2\pi \) and \( h \) is Planck’s constant. Laser intensity is square of the electric field, which is defined as follows:

\[
I(t) = 2\varepsilon_0 c |\vec{E}(t)|^2. \tag{1.1}
\]

Here, \( c \) is the speed of light in free space, and \( \varepsilon_0 \) is the vacuum permittivity. Nonlinear interactions such as two-photon and multiphoton processes are governed by cycle-averaged laser irradiance or intensity \( I_{\nu s} = p / A \), rather than the laser fluence. The laser parameter that captures the pulse duration is average laser power \( \langle P_\nu \rangle = \varepsilon / (\pi^{1/2}\tau) \) (assuming a Gaussian pulse shape); here \( \tau \) is the duration of the pulse. In the ultrafast regime, the electrical energy is packed tightly within the short durations and hence the peak electric fields are extremely high and have the ability to saturate the molecular transitions with the population oscillating at Rabi frequency \( \Omega_i \).

For a typical Nd:YAG-based ns laser with duration of 8 ns, laser energy of 2 mJ, beam diameter of 50 \( \mu \)m, laser intensity is \( 7.2 \times 10^9 \text{ W cm}^{-2} \); whereas, for a Ti:Sapphire-based fs-laser with energy of 6 \( \mu \)J per pulse, pulse duration of 100 fs, and beam diameter of 50 \( \mu \)m, laser intensity is \( 1.7 \times 10^{12} \text{ W cm}^{-2} \). Clearly, with orders-of-magnitude less energy, shorter pulses can be highly efficient for excitation of the plasma species producing stronger diagnostics signal.

In terms of the spectral properties, fs lasers are associated with broad bandwidth (\( \sim 150 \text{ cm}^{-1} \) for a \( \sim 100 \text{ fs-duration pulse} \) to ultra-broad bandwidth (\( >1000 \text{ cm}^{-1} \) for a \( \sim 10 \text{ fs-duration pulse} \)), whereas bandwidth of a 10 ps pulse is \( \sim 2 \text{ cm}^{-1} \). In typical plasma species, e.g. in molecular \( \text{N}_2 \), the ground rovibrational states are separated by \( \sim 8 \text{ cm}^{-1} \). Hence, fs-laser pulses couple many molecular levels simultaneously allowing single-shot spectral measurement of measured species, whereas ns and ps lasers generally couple only one transition at a time, because of their narrow bandwidth. Hence, ns or ps-laser frequencies are scanned to obtain the complete spectra of the target species, or broadband modeless lasers are used to obtain single-shot spectra. Furthermore, fs-laser-based diagnostics measurements are inherently collision independent if the detection time is short, since typical collisional timescales at atmospheric pressure are a few tens of ps to a few hundred ps. From the diagnostics perspective, fs lasers have a myriad of other advantages that are discussed in detail in sections 3.1 and 4.

The overarching goal of this review is to discuss current state-of-the-art ultrafast-laser-based spectroscopic techniques and their remarkable development over the past two decades in meeting at least one or all of the above five goals for the measurement of electric field, temperature, number density of the atomic, molecular, and plasma species. New avenues that resulted from a detailed understanding of plasmas and that aided the validation of plasma models will also be highlighted. Future opportunities of ultrafast diagnostics for characterizing and understanding extreme plasma conditions will also be discussed.

2. Current state-of-the art laser-based approaches for plasma characterization and technical challenges

As outlined earlier, most of the current state-of-the-art optical-diagnostic techniques for plasma characterization rely on light scattering from the reacting plasmas excited mainly by laser pulses with ns duration. Since the development of highly-transient plasmas are sustained by ns-duration voltage pulses, the use of ultrashort-pulse (picosecond (ps)) and fs-laser diagnostics has considerable advantages, as discussed earlier. Ultrashort laser pulses can induce a small optogalvanic effect that influences the electron density in the plasma via the inverse Bremsstrahlung process. However, the ultrashort pulses prevent the generation of cascaded ionization and laser-induced breakdown since the pulsewidth of the laser is
shorter than the collisional timescales at atmospheric pressure or higher [46]. Thus, the nonlinear diagnostics (CARS, FWM, and second-harmonic generation (SHG)) employing ultrashort pulses are typically independent of laser-induced breakdown. In the following, we briefly discuss the current state-of-the-art spectroscopic methods used for the measurement of the key plasma parameters such as electric field, temperature, concentration of plasma species, and flow velocity.

### 2.1. Spectroscopic methods for electric-field measurements

The rapid development of ultrashort-pulse laser diagnostics has made it possible to address several critical challenges in the characterization of highly-transient plasmas. One such challenge concerns the measurement of the spatio-temporal distribution of the electric field in high-peak-voltage pulsed discharges with ns and sub-ns voltage-rise times. These measurements are essential for understanding the kinetics of ionization and charge transport in these plasmas, since rapidly varying electric field and strong spatial gradients (e.g. in fast-ionization wave discharges and streamer discharges) may have a significant effect on the EEDF. In this case, the prediction of both the EEDF and the electron-impact-rate coefficients requires the use of advanced theoretical and modeling approaches such as Monte Carlo–particle-in-cell [47] than the widely used two-term expansion solution of the Boltzmann equation for plasma electrons [48]. Experimental data under these conditions are critical for the validation of these modeling approaches.

#### 2.1.1. Emission spectroscopy

The use of optical-emission spectroscopy for reduced electric-field interference (e.g. based on the comparison of nitrogen second-positive and first-negative emission-band intensities [49]) is affected by two major uncertainties that are rather difficult to quantify. First, the emission-spectroscopy signal is averaged over the line of sight. In many high-pressure air plasmas such as streamers and surface dielectric-barrier discharges, optical-emission spectra are collected across a region with very steep spatial gradients, which necessitates the incorporation of the line-of-sight integration procedure into the data analysis and modeling predictions. This also makes it a challenge to determine whether the two emission bands originate from the same spatial location, which may have a significant effect on the electric-field value inferred from the emission-intensity ratio. Second, the procedure of electric-field inference is typically based on the steady-state solution of the two-term expansion of the Boltzmann equation for the symmetric part of the EEDF [48]. The applicability and accuracy of this approach under the conditions of strong temporal and spatial gradients that are typical for ns-pulse streamers and surfaces are highly uncertain. The higher-order expansion of the Boltzmann-equation solution and Monte Carlo simulations are necessary to estimate the effects of temporal and spatial electron-energy relaxation on the EEDF [50].

#### 2.1.2. Pockels probe

Another electric-field measurement technique based on the use of an electro-optic (Pockels effect) probe has been employed recently. Utilizing the fact that the refractive index is proportional to the applied electric field [51], Pockels probe enabled simultaneous measurements of two electric-field-vector components in a pulsed dielectric-barrier capillary discharge in helium [52]. In this approach, however, the electric field is typically measured outside the plasma, because the insertion of the probe within the plasma perturbs the electric-field distribution [53].

#### 2.1.3. FWM

A nonintrusive laser-diagnostic method of making electric-field measurements in high-pressure discharges is the FWM technique [53], which is similar to CARS (see section 4 for more details). Briefly, in this method, the probe beam used in CARS is replaced by an externally applied electric field that acts as a ‘zero-frequency’ probe wave, generating a coherent signal beam with the wavelength corresponding to the energy difference between the ground and the first excited vibrational state of the molecules [42]. Similar to CARS, the intensity of the IR beam generated from FWM scales quadratically with the electric field and pressure. The duration of the IR signal, which limits the temporal resolution of this method, depends on the coherence-dephasing time of the molecules excited by the pump and Stokes beams, typically of the order of a few hundred ps. Thus, this approach is especially effective for electric-field measurements in high-pressure discharges, such as volumetric and near-surface dielectric-barrier discharges that are sustained by high-peak-voltage ns-duration pulses. Most FWM measurements in plasmas have been conducted on H₂ or N₂ as a probe species using ns-laser systems [54–59]. The use of ns-laser limits the time resolution of this approach and FWM signal intensities are also typically poor, limited by the intensity of the laser. Significant enhancement of the signal compared to the ns approach is achieved when the FWM signal is produced using shorter duration (ps) lasers. Higher signal allows the electric-field measurements of individual electric-field components [60–63] with improved SNR and improved sub-ns temporal resolution [64]. Furthermore, time resolution in the repetitively pulsed-discharge experiments is limited by the voltage-pulse ‘jitter’ (typically of the order of ~1 ns). Higher temporal resolution is achieved by saving the relevant waveforms (voltage, current, pump laser, and CARS signal) for each laser shot and using short-duration ‘time bins’ (of the order of coherence decay time, ~200 ps) during data post-processing [60]. Although measurements in atmospheric-pressure air plasmas using nitrogen as a probe species are considerably more challenging, because of nitrogen’s lower Raman cross-section compared to other plasma species in air [58, 62], they have significant potential for characterizing atmospheric-pressure air plasmas (e.g. see figure 6), with applications in plasma aerodynamics, biology, and medicine as well as high-pressure fuel-air plasmas for plasma-assisted combustion.

#### 2.1.4. SHG

Recently, another nonintrusive laser-diagnostic method for electric-field measurements was demonstrated using SHG by a fs-laser beam passing through an electrostatic electric field in atmospheric air (see figure 7) [65]. This
method is based on the asymmetry in polarizability that is induced by an applied electric field that allows the observation of SHG, which is otherwise forbidden in homogeneous media. The use of an fs-laser with a relatively low pulse energy (∼500 μJ, ∼50 fs pulse duration) considerably increases the SHG signal intensity and prevents laser-induced breakdown. One of the principal advantages of this method is that, unlike FWM, it is species-independent and can be used in many different gas mixtures. Also, it is possible that a detectable SHG signal induced by the electric field can be generated using a ps laser with pulse energy of a few tens of mJ and pulse duration of a few tens of ps.

The electric-field measurements discussed above have been conducted in well-characterized, repetitively pulsed, ns-duration discharges (or repetitively pulsed electrostatic electric fields), with FWM signal accumulated over multiple pulses (of the order of a few hundred). In dielectric-barrier discharges and atmospheric-pressure plasma jets, sustained by more conventional AC waveforms rather than ns-duration pulses, an additional difficulty arises, since these discharges are often generated as an ensemble of micro-discharges that is distributed randomly over space and time. In this case, the measured electric field would represent a value averaged over the laser-beam path unless plasma self-organization occurs [61], forming a reproducible surface-charge distribution and electric-field pattern [66]. Electric-field measurements in ‘single-shot’ discharges with relatively poor shot-to-shot reproducibility (such as isolated streamers or sparks), may require discharge guidance by an auxiliary ultrashort laser pulse [67]. Finally, the spatial resolution of the FWM and SHG methods that employ collinear phase-matching geometries may be fairly low, up to several centimeters along the direction of the laser beam unless a different phase-matching scheme is used [62].

2.2. Measurement of electron temperature and electron density

The second challenge encountered in the characterization of highly-transient plasmas is making nonintrusive, time-resolved, spatially-resolved measurements of electron density and electron temperature and, possibly, EEDF. These measurements are critical for quantitative insight into the electron kinetics and discharge-energy partition both in ns-pulse discharges and in more commonly used dielectric-barrier discharges as well as atmospheric-pressure plasma jets driven by AC, RF, and microwave waveforms. Again, the use of emission spectroscopy for the electron-density inference from Stark spectral-line broadening is hindered by the uncertainty in spatial resolution and by the relatively low temporal resolution. Thomson scattering, which is used for electron-density and electron-temperature measurements in nonequilibrium plasmas, is limited by low SNR that requires signal accumulation over a large number of laser shots in steady-state or repetitively pulsed experiments (∼10^7 laser shots at electron density of ∼10^{11} cm^{-3} [68], ∼10^{-3}–10^{4} laser shots at electron densities of 10^{14}–10^{15} cm^{-3} [69–71]). In addition, the SNR and spectral resolution should be sufficiently high to permit the deconvolution of overlapping Thomson and Raman scattering in high-pressure gas mixtures [69] (e.g. see figure 8). Since the Thomson-scattering signal is proportional to the laser fluence (i.e. the total number of photons passed through the probe volume), the use of ultrashort-pulse lasers would have a rather limited advantage over the more widely used ns lasers. On the other hand, narrow-line-width burst-mode lasers (BMLs) that are operated at high pulse energies and high-repetition rate would offer a significant advantage over lasers operated continuously at pulse-repetition.
rates ranging from a few tens of hertz [68] to a few kilohertz [69–71]. As an example, a recently developed custom-designed laser system generates ~100 ps duration, 0.15 cm$^{-1}$ pulses with pulse energies of up to ~500 mJ/pulse, pulse-repetition rate of ~10 kHz–1 MHz, and ~100–10,000 pulses/burst (total burst energy of ~100 J) [72]. The use of these lasers for Thomson scattering would considerably improve the accuracy of the data collected, which would not be affected by the variation of plasma conditions on a longer timescale. In addition, these lasers are very well suited for nonlinear frequency conversion, because of their inherently high-peak intensity. Their frequency-conversion efficiency (exceeding 50%) is much higher than that of commercial-grade systems and is essential for FWM and CARS measurements, where two or three separate frequency-conversion processes may be utilized for the generation of the necessary laser output.

2.3. Measurement of vibrational-level populations

The third challenge in the characterization of molecular plasmas that are sustained at high-specific-energy loading (e.g. in air or in fuel–air mixtures) is spatio-temporally resolved temperature and vibrational-population measurements. The results provide quantitative insight into the kinetics of ‘rapid heating’ in short-pulse-duration discharges, which is caused primarily by the collisional quenching of the excited electronic states of nitrogen molecules [73–77]. This process is essential in high-speed-plasma-flow control [78, 79] that is driven by localized volumetric heating of the flow in the pulsed discharge [80, 81]. It also has a significant impact on plasma-assisted combustion—in particular, the competition of plasma-generated radical reactions and thermal ignition [82]. The use of emission spectroscopy for the translational–rotational temperature inference (from partially rotationally resolved structure of N$_2$ second-positive emission bands [76, 78, 80, 82]) is hindered by the uncertainty in the spatial resolution and the relatively low time resolution. The use of ultrashort-pulse (ps) CARS spectroscopy, on the other hand, considerably improves both the spatial and the temporal resolutions, along with improved SNR; while improvement in the temporal resolution results from the usage of ultrashort pulses, the spatial-resolution improvement is afforded by proper selection of the phase-matching condition to discriminate the coherent CARS signal beam from the plasma emission and stray light (see figure 9) [83–85]. Comparison of the results of these measurements with kinetic-modeling predictions (see figure 9) identified several dominant kinetic processes that control rapid heating (quenching of electronically excited N$_2$ molecules) and slow heating (vibrational relaxation of N$_2$ molecules by O atoms) in the afterglow of ns-pulse discharges in air [77, 85].

The timescale of the rapid heating process in atmospheric-pressure discharges in air is several ns [82]; thus, resolving it accurately would necessitate the use of ultrashort-pulse-duration (ps and fs) lasers. In high-pressure pulsed plasmas, the SNR of the CARS signal can be sufficiently high to enable single-laser-shot measurements for which the time resolution is limited only by the duration of the laser pulse (e.g. see [3] and references therein). Recent works have demonstrated the capabilities of fs-CARS thermometry in high-pressure environments, including single-shot measurements in atmospheric-pressure flames at 1 kHz [86], single-shot measurements of 1D temperature distributions in flames [87], and time-resolved temperature measurements at pressures up to 50 bar [46]. CARS-based measurements will be discussed in detail in sections 4 and 5.

2.4. Measurement of number density of atomic and radical species

The fourth challenge in the development of diagnostics of chemically reacting plasmas that are sustained in air and in fuel–air mixtures involves time-resolved measurements of the absolute number densities of atomic and radical species and their spatial distributions. The reacting plasmas include both ns-pulse discharges and more commonly used discharges
driven by AC, RF, and microwave waveforms—e.g. atmospheric-pressure plasma jets involving reacting species O, H, and N atoms as well as radicals such as NO, OH, NO2, and HO2 and long-lived metastable species such as O2(a′ Δ). It is well known that the yield of atomic and radical species generated in the plasma is significantly enhanced at high-peak intensities with reduced electric fields, which are typical for ns-pulse discharges. These measurements are critical for plasma-assisted combustion applications and for plasma applications in biology and medicine. Specifically, the generation of O and H atoms as well as OH radicals in nonequilibrium plasmas is essential for the initiation of reaction chains with fuel species, plasma oxidation, and subsequent ignition. HO2 radicals, on the other hand, are much less reactive, and their formation during other radical recombination in high-pressure, low-temperature plasmas is detrimental to plasma-assisted combustion. Furthermore, emission from laser-generated plasmas, known as laser-induced breakdown spectroscopy (LIBS), has been used for measuring ratios of the concentrations of reaction species in a reacting flame under high-pressure (up to 11 bar) conditions [88]. The LIBS-based diagnostics is pursued for ps- and fs-laser excited plasmas in reacting flames [89].

Excited species and radicals are also known to play a significant role in biochemical processes [19]. However, lack of credible in situ characterization of plasma sources—in particular, range and number densities of species generated—has been one of the most significant deficiencies in many previous studies of low-temperature plasmas for applications such as plasma sterilization, wound healing, and cancer therapies. Lack of characterization limits the fundamental understanding of the mechanism of plasma interaction with viruses, bacteria, cells, and tissue. This uncertainty resulted in an ongoing discussion among researchers in the field concerning what may be considered a ‘plasma dose.’ Most previous studies in the field relied on a purely empirical approach, i.e. the generation of unspeficied amounts of reactive oxygen and/or nitrogen species by the plasma near a cell culture or an aqueous solution being perfectly studied to detect and isolate the effect of generated species. Although this approach may have been justified at an early stage, further development of plasma–biomedical applications requires accurate quantitative data on the chemical composition of plasma. Specifically, in plasma–liquid interaction environments, the measurement of fluxes of dominant species generated in the plasma towards the liquid surface is critical.

The accuracy of ‘conventional’ LIF and TALIF employing ns-pulse lasers, which are widely used for radical and atomic-species measurements, is known to be limited to a significant extent by the uncertainty of the collisional-quenching rate of the excited states populated by the laser pulse. The quenching rate may vary significantly with the temperature and chemical composition of the plasma, which is controlled both by plasma-chemical reactions [31, 90, 91] and by mixing and evaporation processes that occur in atmospheric-pressure plasma jets [92] and plasmas generated over liquid surfaces [93]. In addition, laser-induced photolytic effects (photodissociation of molecules) may introduce a significant additional uncertainty into the results. The use of ps and fs lasers with low pulse energies and pulse durations comparable to or shorter than the collisional timescales makes it possible to obtain photolytic interference-free TALIF measurements of atomic-species distributions, as well as direct measurements of the fluorescence quenching rates, which will be discussed in detail in section 3 [44, 94, 95].

Quenching-independent measurements of OH employing fs fully resonant, electronically enhanced CARS (FREE-CARS) have also been demonstrated recently [96], which will be discussed at length in section 6. Comparison of these results with those of kinetic modeling would help the development of predictive-modeling tools and reduce the need for the empirical approach that has been prevalent in previous work in this field.
3. Recent development in fs-laser-based imaging of key reacting species

As outlined in section 1, the spatial distribution and temporal evolution of key intermediate plasma species including ions, neutral metastables, and reactive species are vital to the understanding of plasmas and reacting flows [10]. In particular, quantification of atomic neutrals such as hydrogen, oxygen, nitrogen, and carbon are crucial, because of their high concentrations and reactivities. Many low-temperature and highly nonequilibrium plasma sources, operating in atmospheric-pressure gas and liquid environments [2], are in the initial stages of development. This section contains a discussion of the recent developments in 2D imaging of key species, as mentioned earlier.

3.1. Comparison of ns, ps, and fs-laser-based imaging—their similarities and shortcomings

Noninvasive and in situ laser-based spectroscopic techniques such as LIF are widely used for species-dependent measurements and can be extended to 2D imaging via PLIF in many situations [28]. The LIF-based diagnostics signal is linearly dependent on the species concentration, compared to the quadratic dependency in nonlinear techniques such as in CARS, FWM, etc [97]. Hence, LIF-based techniques are particularly suitable for minor-species imaging [29]. Nevertheless, as discussed in section 1, LIF-based measurements of key atomic species such as H, O, and N as well as molecular species such as CO are particularly challenging, because the frequencies necessary for single-photon electronic excitation fall into the VUV region, where the medium is optically dense in most practical devices and poses a significant problem to propagation through air [27]. Therefore, to avoid strong absorption of the VUV excitation pulse, the excited states of these key species must be accessed through multiphoton excitation [98], which requires visible or ultraviolet (UV) pulses with high pulse peak intensities to overcome the relatively weak multiphoton-absorption cross-sections, as was first shown in H and D atoms [36]. The TALIF technique was dramatically expanded to measurements of other species in reacting flows [99,100] and plasmas [101,102]. TALIF has been employed for diagnostics in a variety of nonequilibrium plasmas [103,104].

Unfortunately, since the two-photon excitation rate scales as the square of the irradiance, all of the ns-laser-based TALIF measurements require high irradiance of visible or UV photons [27]. The high-irradiance excitation causes unwanted photodissociation of other species in the medium, generating the same species that are being probed resulting in significant interference [37-40]. Settersten et al carefully probed the extent of the photolytic interference caused by ns-laser-based excitation for TALIF measurements of the oxygen atom in a hydrogen-fueled laminar diffusion flame using a weak ps probe [105]. The results are presented in figure 10; a 3-GW cm⁻² ns-photolysis laser tuned at 225.58 nm with 3.5 ns duration generates the TALIF signal by exciting the \(3p^3P \rightarrow 2p^3P\) transition of the O atom; and the LIF signal is detected from the \(3p^3P \rightarrow 3s^3S\) transition at 845 nm. The same transition was probed by the 55 ps-duration dye laser tuned to \(J = 2\) line of the \(3p^3P \rightarrow 2p^3P\) two-photon transition. The figure clearly shows significant contribution of photolytic O-atom emission to the TALIF signal, which is not present when the TALIF signal is generated by the weak ps-probe excitation only. The authors also verified that the major contribution of the ns-laser-based photolytic interference in the TALIF signal was caused by photochemical production of the O atom from CO₂, as opposed to photolysis of O₂. A partial suppression of this photolytic interference had been reported for H- and O-atom-detection TALIF schemes using ps-duration pump pulses [41], which emphasizes the potential of ultrafast-pulse excitation in reducing or removing photolytic interferences in the detection of species of interest via TALIF. The advantage of moving towards a shorter pulse arises from the fact that higher irradiance can be realized with orders-of-magnitude lower fluence to obtain a similar level of SNR. Also, it is worth noting here that the threshold of laser intensity for the saturation of dipole excitation is inversely dependent on the square of the pulse duration of the excitation pulse; hence the shorter pulse excitation is preferable to avoid signal saturation [106,107].

Fs-duration pulses, which exhibit high-peak intensities but low average energies, provide three particular advantages: (1) high-peak intensity allowing efficient two-photon excitation; (2) low average energies virtually eliminating photolytic production of additional H or O atoms; and (3) commercially available fs lasers with kilohertz repetition rate offering single-shot diagnostics with TALIF for transient or turbulent environments.

Stauffer et al first demonstrated the fs-TALIF of the radical OH that is produced as a reaction intermediate in a laminar premixed flame [108]. Fs-TALIF-based atomic imaging of hydrogen was demonstrated, and a detailed study of the role of photolytic interference is presented in [109].
Considering TALIF of the H atom, the advantages of transitioning to fs-duration-based excitation can be understood as follows: the two-photon excitation of the $n = 1 \rightarrow n = 3$ transition of the H atom with 205 nm photons is used to populate the $n = 3$ level, and the subsequent H$_2$ fluorescence at 656 nm from the $n = 3 \rightarrow n = 2$ decay is detected. Shown in figure 11 are schematics of several competing processes that can complicate the quantitative interpretation of measured TALIF signals, including three-photon photoionization, SE along the signal-propagation direction, collisional quenching, and photolytic production of additional H atoms that contribute to the observed LIF signal. Typically, photodissociation of numerous H-containing flame radicals and molecules can produce substantial quantities of additional H in the medium. In these conditions, fs-duration pulses become favorable for TALIF, because the signal is proportional to the square of the laser intensity, whereas single-photon-induced photodissociation processes scale linearly. Therefore, high-peak powers but low average energy associated with fs pulses virtually eliminate photolytic interference. In addition, the broad bandwidths of nearly Fourier-transform–limited fs pulses contribute collectively to enhance multiphoton excitation through the combination of a large number of photon pairs with energies summing to the resonant energy of the $n = 1 \rightarrow n = 3$ transition (see figure 11(b)), since all contributing photon frequencies have the same spectral phase [86]. Several studies that have been documented on fs-TALIF imaging of different atoms and reacting intermediates will be discussed later in this section.

Schmidt et al recently investigated the merits of applying the fs-TALIF technique to the measurement of atomic oxygen in an atmospheric-pressure plasma jet (APPJ) source with a helium–oxygen feed gas for direct comparison with conventional ns-TALIF [44]. For this comparison, high-pressure microplasma sources with small characteristic length scales were considered, because of the presence of strong spatial gradients for atomic-species concentration within an order of 100 μm or less. For fs-TALIF, atomic oxygen and xenon were excited by an optical parametric amplifier (OPA) pumped by a Ti:sapphire regenerative amplifier generating ∼25 μJ/pulse at 225 nm for the two-photon atomic transitions. In ns-TALIF, the required UV beam was produced by mixing the output of the dye laser with the frequency-tripled output of the Nd:YAG laser in a beta-barium-borate crystal. The detection system consisted of two main parts: (1) a camera that was used to image the TALIF signal in the discharge volume of the APPJ and (2) a gated photomultiplier tube (PMT) that was used to make point-based collisional-quenching measurements of the excited electronic state. A comparison of ns- and fs-TALIF will now be presented.

3.1.1. Accuracy of quenching measurement. The timescales associated with collisional quenching can vary from a few ps to hundreds of ps, depending on the collisional environment. Thus, accurate calibrations for quantitatively measuring the concentrations of atomic species are limited only to very low-pressure regimes in ns-laser-based TALIF, because of the difficulty in deconvolving the time-resolved fluorescence decay signal from the excitation-pulse envelope (shown in figure 12) [44]. However, in fs-TALIF, the collision is frozen during the excitation enabling direct measurement of the quenching rate following the excitation. As shown in figure 12(a), the effective quenching rate must be extracted from the ns-TALIF signal by modeling the known natural decay rates and the excitation rate. However, fs-TALIF signal can provide a direct measure of the quenching rate from the time-resolved decay of the fluorescence signal.

3.1.2. Significant reduction in photodissociation. As mentioned earlier, the photodissociation or photolysis in ns-TALIF produces significant background interference. In figure 13, the comparison of ns-TALIF and fs-TALIF for atomic oxygen is presented where radial profiles are obtained for 4%-O$_2$/He discharge under the same operating conditions as in figure 12. Clearly, when the ns-pulse energy is increased, the additional off-axis signal increasingly perturbs the normalized O-atom radial profile. With 4% O$_2$, 11 kV applied voltage, and a pulse-repetition frequency of 15 kHz, the He–O$_2$ discharge primarily produces ozone that enshrouds the plasma jet up to ~1 cm from the discharge axis. Since O$_3$ has more than a five-orders-of-magnitude higher absorption cross-section than O$_2$, a higher concentration of O atom is generated within the duration of the ns pulse, reducing the accuracy of the concentration measurement. However, in fs-TALIF, the laser energy has almost no effect on the signal mainly because of the lower laser fluence. The laser fluence in fs-TALIF is orders-of-magnitude lower than the ns system. Since photodissociation linearly scales with fluence, fs-TALIF has a significant advantage of providing higher accuracy in concentration measurement. It is to be noted that the signal level with 2.3 μJ of laser energy is sufficient to perform single-shot measurements for the fs excitation case, whereas even 70 μJ of energy requires.
significant averaging to achieve decent SNR for the ns excitation scheme.

3.1.3. Superiority in 2D-imaging capability. The advantages of high-repetition rate, low average energy, and high irradiance in the fs-laser-based TALIF have also been tested for the planar-imaging capability. Superior 2D images with larger image area averaging over significantly shorter duration are achieved with fs-TALIF compared to ns-TALIF. The images were reconstructed from a vertical scanning of the full image, as shown in figure 14. The time required for reconstruction of the 2D images is significantly less in fs-TALIF (~20 min) than ns-TALIF (>3 h) dictated by higher signal level and kilohertz repetition rate of the laser system. Details of the 2D imaging will be discussed in detail for specific atomic and molecular species in the following subsection.

Furthermore, in recent years efforts have been made to move the development of BML towards generating pulses with shorter durations that have the ability to produce intense pulses up to megahertz repetition rates. The short-pulse BML will pave the way for high-speed (>100 kHz) diagnostics of turbulent reacting and nonreacting flows [72, 110]. Such capabilities with high-energy and high-bandwidth lasers would be extremely useful for investigating transient and turbulent flows. These capabilities could be further extended to 3D measurements and to 4D with temporal evolution recorded [111, 112].

Thus, the benefits of fs-TALIF over ns-TALIF can be summarized as: (1) higher two-photon excitation efficiency, (2) reduction in interference from photodissociation, (3) direct

Figure 12. (a) Atomic-oxygen ns-TALIF signal collected from 2%-O₂/He-mixture APPJ discharge with fast-rise time PMT and 12 ns-FWHM laser-pulse duration, illustrating limitations of ns-duration laser pulses to resolve sub-ns excited-state effective lifetime accurately. (b) Fs-TALIF for similar conditions in (a); the exponential decays demonstrate the strength of fs-duration excitation as collected with high-speed PMT. Reproduced from [44]. © IOP Publishing Ltd. All rights reserved.

Figure 13. Comparison of induced photodissociation levels for different incident laser-pulse energies indicated in the legend for (a) ns-TALIF and (b) fs-TALIF. Independent of incident energy, fs-TALIF shows no discernible levels of induced photodissociation. Reproduced from [44]. © IOP Publishing Ltd. All rights reserved.
measurement of the quenching rates of the excited states that are limited only by the detector bandwidth and not by the pulsewidth of the laser, (4) potential for 2D imaging of atomic species, (5) higher dynamic range, because of a lower single-shot detection limit, and (6) superior measurement precision afforded by the all-solid-state fs-laser systems. Pulse-to-pulse energy fluctuation for fs lasers is typically 2% compared to \( \sim 10\% \) fluctuation for ns lasers.

3.2. Atomic imaging in low-pressure and atmospheric-pressure plasmas

As discussed previously, the measurement of intermediate atomic species such as H, O and N atoms, as well as molecular species such as OH, NO and CO in chemically reacting flows such as plasmas and flames provides key insight into the physical and chemical nature of the system [113]. For example, the generation of O and H atoms as well as OH radicals in nonequilibrium plasmas is essential for the initiation of reaction chains involving fuel species and plasma oxidation, and subsequent ignition. The single-shot imaging capabilities of atomic and molecular species described above will significantly aid in enhancing the understanding of highly-transient reacting flows and their kinetics. In this subsection, we will review the development of the TALIF technique for a few atomic species and molecular radicals of interest for plasmas and reacting flows and discuss the recent developments in spatially and temporally resolved fs-TALIF-based concentration measurements and imaging in detail.

3.2.1. H-atom imaging. Hydrogen atom is a key plasma species that is easily generated, e.g. in a low-pressure plasma discharge by electron-impact dissociation

\[
e + H_2 \rightarrow e + H_2^* \rightarrow e + 2H(1s).
\]  

The H atom generated in the plasma plays a very important role in subsequent reaction chain [113]. Hence, quantitative measurement of the H atom is crucial to the understanding of the chemical kinetics in reactive plasmas. Ever since the first observation of two-photon \( n = 1 \rightarrow n = 3 \) excitation of the H atom by 205 nm laser excitation and detection of fluorescence signal at 656.3 nm was reported by Bokor et al [36], H-atom TALIF has been used as the most effective detection technique and applied to many different plasmas and flames [10]. Using ns-duration laser excitation for TALIF emission, the absolute H-atom concentration is measured in a pure hydrogen RF discharge between a pair of planar electrodes in a parallel-plate configuration [114]. From the temporal evolution of the TALIF signal, the authors observed that the H atoms are produced near both electrodes at the onset of the discharge, but over a period of 2.5 ms, the H-atom concentration becomes flat between the electrodes. The laser-induced dissociation of molecules during the H-atom TALIF measurement is discussed in [115]. Atomic hydrogen is measured using TALIF in a laboratory model of NASA’s hydrogen arcjet thruster, and the hydrogen dissociation fraction was reported to be \( 31\% \pm 14\% \) [116]. TALIF measurement of the H atom in an expanding Ar–H cascaded arc plasma showed that the signal is strongly self quenched [117]. With TALIF measurement in an expanding thermal Ar–H plasma, Boogarts et al proposed to use rare-gas Kr calibration as opposed to a flow-tube reactor method, and the detection limit was reported to be \( 10^{15} \text{m}^{-3} \) [104]. Many
other ns-TALIF measurements of the H atom in plasmas are reported, e.g. in highly diluted SiH4–H2 RF discharges that are used in thin-film deposition [118], in a large-scale microwave plasma reactor [119], in a pulsed microwave discharge [120], in a diamond-depositing DC arcjet [121], in a hydrogen gas flow into a wall-stabilized cascaded arc [122], in helicon plasmas [123], in ns-pulse discharges at a liquid–vapor interface [93], in an Ar–O2–H2 mixture excited by ns-pulse discharges [124], etc. Ns-TALIF suffers from rapid quenching (particularly in higher pressures) and photolytic interferences, as discussed earlier. Recently, Schmidt et al demonstrated that 2D imaging of absolute concentration of the H atom can be achieved using fs-laser-based TALIF [95]. Those authors demonstrated that the high-peak intensity of the fs-laser pulses with low average energy and increased spectral bandwidth compared to that of the ns lasers provides high-fidelity TALIF signal. The 2D TALIF image is obtained in a low-temperature ns-pulse discharge plasma from a ‘canonical’ pin-to-pin geometry at 100 Torr pressure with a 1% hydrogen-in-helium mixture, as shown in figure 15. The presented composite 2D image is generated from 100 shot-averaged images that were collected 25 μs after the onset of the applied discharge voltage. The concentration of the atomic H peaks within ~1.5 mm of the cathode, as shown in the axial distribution of the generated H atom (shown in the left side of figure 15). Note that the absolute concentration of the H atom is obtained by calibrating the signal with Kr, where the absolute number densities ranged from $2 \times 10^{12}$ cm$^{-3}$ to $6 \times 10^{15}$ cm$^{-3}$. It is also reported that the spatial extent of the atomic H is extended in the He mixture compared to the Ar mixture. Selecting the TALIF signal from a small 400 × 400 μm region in the middle of the plasma volume, the temporal decay of the atomic-hydrogen number density is obtained for two separate mixtures, 1% H2/He and 1% H2/Ar. It is shown that the decay rate of atomic hydrogen in the H2/He mixture is slower than that in the H2/Ar mixture.

In reacting flames, H-atom TALIF imaging has been investigated using ps- and fs-laser excitation. From the fs-TALIF line profiles of the H atom in a CH4/O2/N2 Bunsen flame, it is shown that the line-profile shape is independent of the pulse energy, unlike the previous ps- and ns-TALIF experiments—confirming the absence of photolytic interference in fs-TALIF signal [109]. Quantitative measurement of the H atom in more complex, laminar, premixed tubular flames has been demonstrated, offering data to validate the pseudo-1D model for tubular premixed flames [125]. Furthermore, by developing an efficient fourth-harmonic, generator-based, high-power fs UV source for the two-photon excitation (2 × 205 nm) of the H atom, 2D TALIF has been demonstrated in a laminar Bunsen flame [126].

3.2.2. O-atom imaging. Like the hydrogen atom, the oxygen atom is also a key reacting atomic species in the chemical kinetics of most plasmas. The O atom is responsible for the production of reaction intermediates, such as OH and NO, that advances the reaction chain in plasmas. Hence, quantitative 2D imaging of the O atom gives crucial information on the plasma kinetics. The O atom can be generated in atmospheric plasma by electron impact

$$e + O_2 \rightarrow O^- + O$$
$$e + O_2 \rightarrow e + O + O. \quad (3.2)$$

McIlrath et al were the first to show the possibility of using the two-photon transition $2p^3P \rightarrow 3p^3P$ of the O atom for
TALIF-based concentration measurements [127]. Following that demonstration, numerous ns-TALIF-based O-atom measurements have been reported in a variety of plasmas; e.g. a plasma-etching environment [101], a microwave discharge [128], an APPJ [129], a corona discharge [130], methane–air and ethylene–air nonequilibrium plasmas [131], a streamer discharge afterglow [132], an RF-discharge cell [133], a diffuse-filament electric discharge and afterglow [134], ns-pulse discharges in combustion mixtures [135], a capillary ns discharge [136]. However, ns-TALIF of the O atom is plagued by significant photolytic interference [129, 130]. The primary contribution (90%) to photolytic interference in O-atom signal is caused by [10]

$$\text{O}_3 + h\nu \rightarrow \text{O}^3\text{D}) + \text{O}_2(a^3\Delta_g).$$

(3.3)

Since a large amount of ozone is produced in atmospheric plasmas, the dissociation produces significant interference in ns-TALIF signal of the O atom [129].

Recently, fs-laser-based TALIF measurements have been extended to obtain the spatially and temporally resolved O-atom distribution in a ns, repetitively pulsed, externally grounded APPJ in a capillary-dielectric-barrier-discharge (CDBD) configuration flowing helium with a variable-oxygen admixture [94]. Calibrating the signal and imaging system with Xe that has similar two-photon transition frequencies to the O atom, the absolute O-atom density could be obtained. With their setup, 2D planar imaging of the O atom has been demonstrated, with number densities varying by three orders-of-magnitude and a detection limit of $2 \times 10^{12}$ cm$^{-3}$; see figure 16. It is reported that when the concentration of the O$_2$ in the feed gas was changed, a transition was observed in the discharge morphology from annular to filamentary. Furthermore, as shown in figure 17, a planar fs-TALIF image of the O atom was also obtained for the same setup as in figure 15 (discussed in the previous subsection) with a different mixture of 1%-O$_2$/He at 100 Torr in the ‘canonical’ pin-to-pin geometry [95]. The O-atom concentration is surprisingly found to be highest near the anode, which is inverted compared to the distribution of the H atom (figure 15). This inverted O-atom density distribution is attributed to dissociation of metastable excited electronic states of O$_2$, both by electron impact and quenching of excited helium atoms. It appears that these low-energy excited states could be produced more efficiently near the anode.

A detailed comparison and analysis of ns-TALIF versus fs-TALIF of the O atom has been presented for the APPJ discharge configuration in a 4%-O$_2$/He mixture [44], which is discussed in detail in sections 3.1.1–3.1.3. The advantages of fs-TALIF specific to O-atom imaging inferred from this study are: (1) fs-TALIF signal is found to be 15 times stronger than ns-TALIF signal when the signals are normalized with respect to the incident laser intensity, (2) fs-TALIF allows measurements over a wider range of pressures than ns-TALIF, (3) experimental uncertainties in O-atom densities are notably smaller using fs-TALIF ($\pm 17\%$) compared to ns-TALIF ($\pm 33\%$), and (4) 2D O-atom images can be acquired in minutes with fs-TALIF compared to multiple hours with ns-TALIF.

In reacting flames, Settersten and co-workers compared ns- and ps-TALIF of the O atoms to demonstrate the photolytic-interference-reduction advantage for short-pulse laser excitations in a flame [41, 105]. Note that the ns- and ps-laser-based TALIF measurements of the O atom in flames are also not completely free from photolytic interference. In reacting flames, the O atom is primarily generated from photodissociation of the vibrationally excited CO$_2$. Photolytic-interference-free 2D imaging of the O atom is demonstrated with fs-TALIF at a kilohertz rate for a range of CH$_4$–air conditions in a Bunsen flame [137].

3.2.3. N-atom imaging. Nitrogen-containing plasmas are prevalent in many applications. Electron impact can generate nitrogen atoms N($^4S$) easily by direct dissociation.
of ground-state N\textsubscript{2} molecules,
\[ \text{N}_2(X) + e \rightarrow \text{N}(^3\text{S}) + \text{N}(^4\text{S}) + e. \] (3.4)

At low temperatures, charge exchange reaction between N\textsuperscript{+} and N\textsubscript{2}(X) and dissociative recombination of the molecular ion are also very favorable, e.g.
\[ \text{N}^+ + \text{N}_2(X) \rightarrow \text{N}(^3\text{S}) + \text{N}_2^2 \]
\[ \text{N}_2^2 + e \rightarrow \text{N}(^4\text{S}) + \text{N}(^4\text{S}). \] (3.5)

Nitrogen atoms are also crucial in reactive kinetics, because they contribute to the production of intermediates such as NO\textsubscript{x}.

Bischel \textit{et al} have demonstrated that the two-photon 2P\textsuperscript{3}S\textsuperscript{0} \rightarrow 3P\textsuperscript{4}S\textsuperscript{0} transition of the N atom can be excited using 211 nm and the TALIF signal is generally acquired at 869 nm \cite{99}. N\textsubscript{2} TALIF is employed to study flow characteristics in free-nitrogen plasma that was created by cascaded arc \cite{138}. The pressure dependence of N-atom recombination probability is studied using ns-TALIF-based measurement \cite{139}. N-atom TALIF in an atmospheric-pressure pulse corona discharge is measured to investigate the production mechanism of atomic nitrogen \cite{140}. Since the N atom is responsible for the generation of NO, a combined study of NO LIF and N-atom TALIF is carried out in diffuse-filament electric discharge, and it is concluded that NO formation in the ns-pulse discharge is dominated by reactions of excited states of nitrogen \cite{134}. The study is further extended to determine the effect of nitrogen on ns discharges in air, H\textsubscript{2}–air and C\textsubscript{2}H\textsubscript{4}–air mixtures by measuring N-atom TALIF \cite{141}.

All of these N-atom TALIF measurements are limited to ns excitation. With fs-TALIF it is expected that more accurate and higher-dimensional imaging can be realized, which will be crucial for understanding the plasma kinetics.

3.2.4. Other radicals and molecule imaging (OH, NO, CO). Radicals and molecules such OH and CO and the generation of regulated pollutants such as NO are of significance to the diagnostics of reacting flows and plasmas as well. Because of their importance, these molecules have been extensively studied by employing both ns-laser–based LIF and PLIF in a variety of plasmas \cite{33, 34, 93, 142–144} and ps-time-resolved LIF \cite{134, 145}. Settersten, Dreizler, and Farrow used ps-TALIF to measure temperature-dependent and collision-partner-dependent quenching cross-sections of the CO in a heated cell \cite{134, 146}. The development of sub-ps-laser-based LIF, however, holds promise for time-gated detection of molecular species on timescales much shorter than typical collisional lifetime, even at higher pressures. These approaches may, therefore, enable time-resolved, single-shot, and high-repetition-rate LIF or PLIF measurements (in addition to the photolytic-interference-free advantage, as discussed earlier).

Broadband TALIF measurement was first demonstrated in OH to investigate its viability of fs-TALIF for minor-species detection \cite{108}. Stauffer \textit{et al} modeled two-photon absorption in the OH A\textsuperscript{2}Σ\textsuperscript{+} ← X\textsuperscript{2}Π electronic transition involved in the TALIF measurement and showed that the
temperature-dependent initial population is needed for accurate derivation of the relative concentrations from the observed TALIF signal. Recently, planar (2D) photolytic-interference-free fs-TALIF imaging of CO using the $B^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$ electronic transition was demonstrated in a near-adiabatic methane–air flame stabilized over a Hencken burner. Figure 18(a) shows the normalized spectrally-resolved TALIF signal of CO at three different heights of the flame, as recorded with an intensified charge-coupled device (CCD). Visualization of the transient dynamics of the jet flame was captured in the single-shot planar TALIF images presented in figure 18(b). From the photolytic interferences observed, it was concluded that the laser should operate below an intensity of $10^{10}$ W cm$^{-2}$ to avoid interference. This study demonstrated the ability to obtain photolytic-interference–free 2D TALIF images of reaction intermediates at $1 \text{ kHz}$ or higher repetition rate.

4. Recent development in fs-CARS for temperature and species concentrations: advantages of ultrafast CARS

Amongst the various nonlinear spectroscopic techniques discussed earlier, CARS spectroscopy has emerged as the most useful technique for measuring a wide range of the plasma and flow parameters (e.g. temperature, number density of species, and electric field) with high spatial and temporal resolution. The advantages of CARS over other laser-diagnostic methods that were discussed earlier are: (1) high spectral selectivity that results from the CARS signal being generated only from the species that are in Raman resonance with the pump and Stokes beams (i.e. $\omega_k = (E_1 - E_2) / h$), (2) coherent laser-like signal dictated by the phase-matching criterion, removing any interference from the interrogating laser pulses, (3) low absorption of interacting laser beams and generated signal that results from their being individually off-resonant from the electronic transitions and, hence, not absorbed by the medium, (4) capability to probe high-density environments or major species in the target volume that is enabled by the fact that the CARS signal is quadratically dependent on the number density of the target molecule, and (5) high spatial resolution resulting from the Raman interaction mediated by multiple laser beams, generating CARS signal at the interaction volume.

In a typical CARS configuration, like all FWM techniques, photons from three laser beams interact via nonlinear interaction with the target species to generate the fourth anti-Stokes laser-like signal beam, while the first two laser beams, pump ($E_1$) and Stokes ($E_2$) interact via two-photon resonance with the Raman (vibrational or rotational) transition to generate the coherence $\omega_k$ in the probe medium. The third pulse, a probe pulse $E_3$, interrogates the coherence, generating the laser-like coherent anti-Stokes signal $E_4$, as shown in figure 19(a). It has been recognized from the late 1970s that
the CARS technique is capable of generating a highly species-specific and directional signal, because of the unique arrangement of the lasers in a so-called BOX-CARS geometry, where the pump, Stokes, and probe beams coming from three different directions with their wave vectors $k_p$, $k_s$, and $k_d$, respectively, intersect at the interaction region to generate the signal beam precisely at a fourth direction $k_4$ following the phase-matching condition

$$k_p - k_s + k_d = k_4. \tag{4.1}$$

The CARS signal is calculated from the Maxwell equation using standard approximations where the slowly varying envelope of the instantaneous CARS signal can be calculated as [3]

$$I_{\text{CARS}}(t, L) = \frac{e}{c} k_4^2 L^2 |P_0^{(3)}(t, L)|^2. \tag{4.2}$$

Here, $P_0^{(3)}$ is the third-order molecular polarization that is induced by the excitation laser pulses, and $L$ is the interrogation length at the target where the effective nonlinear interaction takes place. The temporal evolution of molecular polarization $P^{(3)}$ is obtained by expanding the source term in the Maxwell wave equation, which can be written as

$$P^{(3)}(t, \tau) = E_3(t) \int_{-\infty}^{\infty} \chi^{(3)}(t')E_1(t + \tau - t') E_2(t + \tau - t') dt'. \tag{4.3}$$

Here, $\tau$ is the delay of the probe pulse with respect to the arrival of the time-overlapped pump and Stokes. Calculation of the third-order susceptibility $\chi^{(3)}$ involves solving the coupled differential equations using the Schrödinger wave equation in a perturbative approach [148] or the density-matrix equations [149, 150]. Furthermore, the ultrafast time-resolved CARS signal is typically measured as an integration of the above polarization for a fixed probe delay $\tau$ to obtain [151]

$$I_{\text{CARS int}}(t) = \int_{-\infty}^{\infty} |P^{(3)}(t', \tau)|^2 dt'. \tag{4.4}$$

Except for very specific limiting cases, the above integration is calculated numerically.

The significance of fs-CARS spectroscopy has been discussed and CARS has been employed for studying gas-phase molecules over the past two decades [151]. The potential advantages of fs-CARS in plasma diagnostics and imaging were first outlined in the review article by Zheltikov [152]. Since that time, fs-laser technology has matured so that current systems can provide energy in excess of 1 mJ or higher at a rate of 10 kHz. The high energy, stability, and tunability via the OPA of amplified fs-laser pulses have opened many new avenues for providing insight into the flow physics of plasmas and reacting flows with unprecedented temporal resolution. A typical fs-CARS setup is presented in figure 20.

A few of the distinct advantages of ultrafast CARS will now be discussed in further detail.

4.1. Multiphoton excitation for stronger coherence

Raman excitation being a two-photon process, fs-laser-based pump and Stokes provide unique advantage over other long-pulse laser-based CARS configurations, because of the associated frequency bandwidth of these pulses. For example, rovibrational lines of molecular nitrogen are separated by $\sim 2320 \pm 20 \text{ cm}^{-1}$; in a traditional ns-CARS configuration, such Raman transitions are typically accessed by using 532 nm laser as the pump and a tunable broadband dye laser as the Stokes pulse. Thus, the Raman-resonance condition $\omega_R = (E_p - E_s)/h$ is satisfied by only one pair of photon energies from each pair of pump and Stokes pulses (see figure 21(a)). However, with fs pulses having a spectral width of the order of 10 nm ($\sim 200$–$300 \text{ cm}^{-1}$), the Raman condition is satisfied by many pairs of photons having different frequencies within the broadband pulses, as depicted in figure 21(b). Thus, a strong Raman coherence [149] is generated with modest excitation-pulse energies through utilization of the full bandwidth [153, 154] and, hence, a stronger signal [3, 149, 155]. The broad bandwidth has also enabled coherent detection of multiple species simultaneously [156]. This multiphoton excitation advantage of fs-laser-based pumping is not limited to CARS but is applicable to any diagnostic method involving multiphoton laser excitations, as discussed in section 3.

4.2. NRB-free detection

One of the major issues with the early works in frequency-domain CARS spectroscopy was the contribution from NRB, which generally appears at the CARS signal frequency. NRB signal is generated when the pump, Stokes, and probe pulse time-overlapped in time at the target volume. This added greater complexity, particularly for high-pressure conditions where the broadening conditions are not well known. The utilization of pulse sequencing with shorter pulses was proposed to remove the NRB in condensed-phase systems [157]. In 2005, Roy et al. showed that with the ability to delay the probe from the pump and Stokes pulses when their durations are 100 ps or shorter, the NRB-free CARS signal can be extracted (see figure 22 [158]). Time-resolved nonresonant signals were obtained by flowing pure O$_2$, CO$_2$, and Ar; and the resonant-CARS signal was acquired for the Q-branch transition in the $v = 0 \rightarrow v = 1$ band of N$_2$ as a function of the time delay between the probe and time-overlapped pump-Stokes pulses. It was observed that the magnitude of the nonresonant signal decreased by three orders-of-magnitude relative to resonant-CARS signal when the probe was delayed by $\sim 110$ ps. Note that the pump and probe-pulse durations were $\sim 135$ ps and that the Stokes duration was $\sim 106$ ps. The NRB suppression is easily extended to fs-CARS diagnostics [159].

4.3. Saturation-free fs-CARS spectroscopy

The intensity of the generated CARS signal grows linearly with the intensities of the pump, Stokes, and probe pulses in the weak field limit. It is well known, however, that in ns-CARS, the Raman coherence can saturate and experience a
Stark shift, modifying the spectral lineshape of the CARS signal at peak intensities above $10^{14} \text{W m}^{-2}$ [160]. However, it has been shown theoretically that in vibrational and rotational fs-CARS studies of gas-phase nitrogen, the threshold of laser intensities for saturation are significantly higher compared to those of other fs nonlinear processes (such as filaments, etc); hence, fs-CARS signal will rarely be saturated [150]. This saturation-free regime for higher intensities has been exploited to increase the CARS sensitivity up to single-molecule conditions in plasmonics [161] and to reach super-spatial and -spectral resolutions in vibrational CARS-microscopy imaging [162].

Also, it has been shown that in an electronic-resonance-enhanced CARS (ERE-CARS) configuration, where the probe pulse resonantly couples the ground and electronically excited electronic states of the molecule, a strong ns-duration probe can saturate the signal [163]. However, in a detailed theoretical study of ERE-CARS for different pulse regimes with durations ranging from 10 ns–10 fs, it was shown that the signal saturation threshold associated with probe pulse begins to increase for pulse durations shorter than the molecular decay and dephasing times; the threshold intensity was shown to increase quadratically with the inverse of the pulse duration [164]. It has also been shown that the saturation threshold of the pump and Stokes intensities for Raman coherence using ultrafast pulses has a similar dependence [106]. The saturation-free regimes in standard fs-CARS or high-saturation-threshold regimes in ultrafast ERE-CARS are

![Figure 20. Typical fs-CARS setup where photons from three beams (pump, Stokes and probe) interact at the target region to generate CARS signal. The laser and optical components with the typical laser parameters marked in the figure are used in [86]. Reproduced with permission from [86].](image)

![Figure 21. Raman excitation of N2 rovibrational line (a) ns-CARS, (b) fs-CARS configurations. Because of multiple-photon pairs of excitation with fs-laser, Raman coherence $\rho_{ab}$ is almost two orders-of-magnitude higher than ns-CARS. Reproduced with permission from [153].](image)
Figure 22. Time-resolved NRB and resonant-CARS signal. NRB falls off rapidly once all pulses move out of the interaction region. Hence, resonant-CARS signal three orders-of-magnitude smaller NB can be retrieved with delayed probe pulse. Reproduced with permission from [158].

helpful in achieving high SNR. ERE-CARS and all-resonant fs-CARS will be discussed in further detail in section 6.

4.4. Collision-independent CARS signal

Collisional quenching of the population and dephasing of the Raman polarization are the major drawbacks in spectroscopy with long-pulse (ns or longer) excitations. Since collisional timescales range from tens of ps to ns, in a long-pulse (ns or longer) CARS configuration, several collision cycles can occur, causing collisional energy transfer of population and dephasing of coherence during the interrogation period that will require accurate collisional modeling to extract the desired diagnostic information. However, in fs-CARS, the signal is generated in timescales where the collisions are almost frozen. This collision-independent signal enables time-resolved studies of vibrations and rotations in gas-phase molecules, which were first conducted by Hayden and Chandler in benzene and 1,3,5-hexatriene gases [151]. Motzkus and co-workers have shown from the beating structure of the experimental transients of H2 that the rotational dynamics could be accurately modeled. Such features could be used to extract detailed information on the J-dependent collisional broadening, line-shifting coefficients, and other molecular parameters, even at high temperature [165] and pressure [159, 166].

Wrzesinski et al investigated the collisional sensitivity of time-resolved fs-CARS by measuring the N2 spectra for various pressures ranging from atmosphere to 50 bar both for pure gas and for gas mixtures (i.e. with different collisional partners) [46]. It was observed that the time-resolved signal at early delays did not exhibit any dependence on the system pressure, as shown in figure 23. For pressures of 1–5 bar, rotational recurrences are observed at longer delays, because of rephasing of a subset of Q-branch transitions of N2 [167]. The overall signal initially decays at the frequency-spread-dephasing timescale [168] (see section 5.2 for more details), but the signal decay at a longer probe delay is governed by the molecular-collision timescales. However, the timescales of such long-time recurrences become shorter with pressure and the recurrences disappear for pressures above 20 bar. Clearly, the CARS signal is collision independent within the first 10–15 ps for pressures up to 40 bar. The modeling of high-pressure data with the exponential-gap energy-corrected-sudden (ECS-E) scaling law required inclusion of the line-mixing effect, as suggested by Knopp et al [167, 169]. Fs-CARS has also been used to demonstrate collisional-interference-free measurement of temperature in high-pressure cells [170]. Such collision-independent fs-CARS can be transitioned to diagnostics of high-pressure and high-temperature plasmas containing ions and neutrals.

4.5. Kilohertz- to megahertz-rate sources

Until the end of the previous century, time-resolved fs-CARS had been developed using a multipass, dye-amplified laser pumped by a Nd:YAG laser operating at tens of hertz [151]. However, this slow repetition rate is not suitable for highly-transient reacting flows or plasmas, where the temperature and species concentration vary rapidly in both the spatial and temporal domains. With the availability of regenerative Ti: Sapphire amplifiers that generate high-energy pulses (up to 10 mJ/pulse) at kilohertz (or higher) repetition rates, high-speed diagnostics have been demonstrated in reacting flows [86] and even in unsteady flow conditions [171]. In the first demonstration of 1 kHz, single-shot fs-CARS thermometry by Roy et al [86], time-resolved N2 spectra were obtained in an atmospheric-pressure, near-adiabatic H2-air flame stabilized over a Henckken flame. The single-shot spectra and associated probability-density functions (PDFs) of the extracted temperature from 1000 spectra for equivalence ratios Φ of 0.5 and 1.0 are shown in figure 24. For the temperature range of 1000–2400 K, the accuracy of the measurements is found to be ∼1%–6% of the adiabatic flame temperature and the precisions are ∼1.5% of the mean temperature. The use of high-energy fs lasers has also enabled 1 kHz rate, 1D (line) [87] and 2D (planar) [172] CARS imaging, as will be discussed in section 4.6.

Recent years have seen the rapid improvement of BML technology to produce high-intense pulses at repetition rates
up to megahertz [72]. The high-energy BML has enabled 3D measurements of LIF in reacting flows and also extended to 4D with temporal evolution recorded [111, 112]. Recent developments have pushed BML towards generating pulses with shorter durations that have the ability to produce intense pulses up to megahertz repetition rates. The short-pulse BML will pave the way for high-speed (>100 kHz) diagnostics of turbulent reacting and nonreacting flows [72, 110]. Such capabilities with high-energy and high-bandwidth lasers would be extremely useful for investigating transient and turbulent flows. These capabilities could be further extended to higher-dimensional CARS measurements, which will be discussed in detail in section 4.6.

4.6. Extending CARS measurements to multiple spatial dimensions: 1D (line) and 2D (plane) measurements

As noted earlier, CARS is an intensity-driven nonlinear process; hence, fs lasers are well suited for the generation of stronger Raman coherences and CARS signal. With the availability of fs lasers that can produce a few mJ/pulse, it has been possible to create laser sheets for performing instantaneous multidimensional imaging based on CARS spectroscopy. 1D and 2D measurements can be extremely valuable in understanding the spatio-temporal instabilities in practical combustion devices with turbulent flows and in aiding the validation of complex turbulent plasma and flow models.

For 1D-CARS, laser sheets are produced by a combination of cylindrical and spherical lenses, arranged in a BOX-CARS setup such that all three beams intersect on a line at the burner and generate the line-CARS signal [87], as shown in figure 25(A). Note that a chirped-probe beam was used to obtain the spectrally- and spatially-resolved line image presented in figure 25(B) (details of the chirped-probe CARS will be discussed in section 5. The CARS line imaging of N2 is presented for room air and a H2–air flame in (a) and (b), respectively. Single-shot temperature measurements at 1 kHz repetition rate are reported in a flat-flame field up to 2000 K, suggesting the possibility of realizing fs-CARS line imaging based on high-speed thermometry in turbulent flames. Kliwer et al demonstrated line-temperature and O2:N2 concentration ratio employing ps-laser-based dual-broadband pure-rotational CARS [173]. The reported accuracy and precision for a temperature range of 410–1200 K were comparable to those of ns-laser-based dual-broadband pure-rotational CARS and 1D vibrational CARS.

Recently, Bohlin and Kliwer demonstrated that the dimensionality of detection for the CARS signal can be extended from 1D imaging to 2D imaging [174], and the laser powers were sufficient to obtain single-shot 2D CARS images [175]. Planar CARS at a 1 kHz rate was demonstrated in a heated jet by Miller et al [172]. These 2D-imaging efforts employed a variant of ultrafast CARS that is referred to as hybrid fs/ps-CARS, where a single broadband, transform-limited fs pulse acting as both pump and Stokes pulses excite many rotational or vibrational Raman transitions and a
narrowband (typically ps duration) probe interrogates the broadband Raman coherence to generate the spectrally-resolved CARS signal \[176, 177\]. Using such a two-beam CARS configuration, the planar temperature map of a pre-mixed laminar CH<sub>4</sub>-air flame has been obtained from N<sub>2</sub> and O<sub>2</sub> rotational CARS, as shown in figure 26 \[175\]. The ability to perform accurate 2D temperature measurements for temperatures in the range 450–2000 K in combination with single-shot data acquisition at high-repetition rates would aid the understanding of the flow physics of plasmas and flames, even in turbulent environments.

In the following section, we present in-depth discussion on how the unique capabilities of the ultrafast CARS described above have been employed to measure temperature and species concentrations in reacting plasmas and flows.

5. Interference-free temperature and species-concentration measurements

As noted in the previous section, the coherent nature of the CARS signal generated from a small, targeted, nonlinear interaction volume eliminates the large background from fluorescence, chemiluminescence and laser scatters that could interfere with the signal. Furthermore, as discussed in section 4.2, it was recognized during the very early development of CARS that employing short-pulse lasers was very useful for suppressing the NRB by the time-delayed interrogation \[157, 178, 179\]. Hence, ps-CARS spectroscopy was extensively used for spectrally-resolved probing of the dephasing dynamics in solid and condensed-phase systems \[180\]. Tunkin and co-workers exploited the NRB-suppression advantage associated with ps-CARS for the spectroscopic interrogation of gas-phase molecules \[181\]. However, the challenge remained from the fact that most of the ps-CARS systems employed synchronously pumped dye lasers running at limited repetition rates (10–30 Hz) and, hence, were not suitable for high-speed dynamics in rapidly changing reacting products in plasmas and reacting flows.

It should be noted that gas-phase temperature measurements rely on the temperature-dependent initial Boltzmann distribution in the microscopic (rotational or rovibrational) states of the molecules. At an equilibrium temperature \(T\), the number density of a target molecule \(n_i\) in a molecular state...
\( n_i = \frac{N}{Q} g_i \exp\left(-\frac{\hbar \omega_i}{k_B T}\right). \)  

Here, \( N \) is the number density of the target molecule in the probe volume, \( g_i \) the degeneracy of the molecular level, and \( k_B \) the Boltzmann's constant. The partition function \( Q \) is given by

\[ Q = \sum_i g_i \exp\left(-\frac{\hbar \omega_i}{k_B T}\right). \]

Hence, to obtain an accurate temperature in a rapidly evolving reacting flow, it is important to obtain single-shot measurement data that can simultaneously excite multiple rotational or rovibrational states for parametrically generating the CARS spectra. In the ns excitation regime, the narrow bandwidth of pulses can couple only one or a few of those ground-state molecular states that are needed for inferring the thermometric information. Alden et al demonstrated that employing a broadband modeless dye laser pumped by Nd:YAG laser with ns duration can simultaneously capture the full spectrum of the Boltzmann distribution in each of the laser shots to achieve single-shot CARS thermometry. For the next two decades, numerous works were reported with different variants of the broadband ns-CARS for thermometric measurements. However, the NRB in the ns-CARS significantly limits the accuracy and degrades the sensitivity of temperature measurement, in addition to the other limitations of the ns-CARS as discussed earlier. Roy et al proposed the use of ps-laser-based CARS to demonstrate NRB-interference-free, single-shot, gas-phase thermometry. Those results were followed by many other investigations in reacting plasmas and flows, which will be discussed in detail in the following subsections.

Although ps-CARS could provide the time-resolved, NRB-free CARS for extracting thermometric information, the measured signal is still strongly dependent on collisions. Hence, accurate modeling of collisional parameters is required for ps-CARS thermometry; but those parameters are
not well known in most of the highly reacting flows. Hayden and Chandler were the first to show the potential application of fs-CARS for gas-phase diagnostics by obtaining time-resolved CARS of gas-phase benzene and 1,3,5-hexatriene, demonstrating a significant Raman-shifted signal with modest laser energies (∼10 μJ) [151]. The collisional independence of the signal was demonstrated by Lang et al [166]. The low energy and high-peak intensity afforded by the fs-laser pulse are well suited for nonlinear techniques such as CARS. Hence, from the early twenty-first century, fs-CARS has been employed in a wide variety of studies in reacting flames and plasmas.

In the following subsections, we discuss different CARS techniques utilizing the distinct advantages of the ps and fs lasers to obtain interference-free temperature and species-concentration measurements.

5.1. Pure-rotational CARS (ps, fs, fs/ps)

At a given temperature $T$, the Boltzmann distribution (5.1) determines the rotational population distribution $n_J$ corresponding to the rotational number $J$ within a given vibrational manifold, and can be written as [28]

$$n_J = \frac{N}{Q_J} g_J (2J + 1) \exp[-BJ(J + 1)\hbar c/k_B T],$$

(5.3) where $g_J$ is the nuclear-spin degeneracy for nonzero nuclear spins, $B$ the rotational constant of a given molecule, and $Q_J = k_B T/(\hbar c B)$ the partition function for rotation. Note that the Boltzmann distribution is an accurate temperature in the equilibrium conditions. However, in nonequilibrium conditions, the measured rotational temperature can be different from the vibrational temperature (to be discussed in section 5.2), because the rotational states equilibrate much faster than the vibrational states, and hence it is assumed that rotational temperature is also representative of the translational temperature in highly-transient plasmas (see section 5.4 for more details).

The rotational population distribution is spectroscopically measured and the rotational temperature is extracted using equation (5.3). Typically pure-rotational CARS (RCARS) signal is an order-of-magnitude stronger than that of vibrational CARS, because the Raman cross-section of pure-rotational transitions is generally higher than that of the vibrational transition lines [28]. RCARS has been extensively used for measurements of gas-phase temperatures employing ns lasers [3]. Seeger et al reported the first demonstration of NRB-free RCARS thermometry employing ps lasers to measure the time-resolved $N_2$ in air and in a laminar CH$_4$ diffusion flame [183]. However, it was observed that the spectrum changes significantly within a short period of time when the probe pulse is delayed with respect to the time-overlapped pump and Stokes pulse, because of molecular collisions; hence, without a detailed time-dependent model, it was difficult to extract temperature from the time-delayed spectrum. In another study, it has also been demonstrated that the interferences from the broadband signal produced by other FWM pathways within the species of interest and also those from other molecules can be reduced by tuning the time delay between the probe and time-overlapped pump and Stokes pulses [184]. Time-resolved dual-broadband ps-RCARS has been demonstrated for thermometry and major-species-concentration measurements in a laminar, nonpremixed sooty flame using a polarization-based interference-suppression technique [185]. Ps-RCARS has also been extended to obtain 1D thermometry and the $N_2/O_2$ ratio in flames [173] and to measure the self-broadening of the J-dependent $N_2$ Raman linewidths directly for a temperature range of 294–1466 K [186]. Similar state-specific linewidth measurements have been made using the pure-rotational (S-branch) transitions of self- and $N_2$-broadened C$_2$H$_2$ [187] and CO$_2$ [188].

The temperature distributions within plasmas are critically important to aid in bracketing the total thermal effects of the pulsed discharges as well as to better determine the production methods of the atomic species and to help support diffusion-rate calculations. Zuzeek et al have employed ps-RCARS for thermometry in low-temperature plasma-assisted combustion in a repetitive ns-pulse discharge (at a 40 kHz pulse-repetition rate and 10 Hz burst repetition rate) in an ethane-air flame operated under fuel-lean conditions and experimentally observed the higher heating rate in the fuel–air plasma compared to the air plasma [189]. Ps-RCARS has also been used in a similar nonequilibrium plasma system to obtain the time-resolved rotational temperature and the $O_2$ mole fraction [190]. A comparison of the rotational temperatures obtained from ps-RCARS in a pulsed-ns-discharge plasma in air and in a flame with different equivalence ratios is presented in figure 27. It is observed that the temperature declines after a subsequent burst of pulses hitting the flame for the $\Phi \geq 0.5$ condition, and from kinetic-modeling
calculation, it is clear that the removal of radicals in a pulsed-discharge plasma completely blocks subsequent exothermic reactions, which renders ignition impossible. In a recent study, time- and spatially-resolved temperature measurement have been demonstrated in ns-pulse discharges in air and H₂–air mixtures employing ps-RCARS of N₂ to study kinetics of energy thermalization [85]. The authors have observed two distinct thermalization regimes: (1) the rapid heating was found to be caused by collisional quenching of electronically excited N₂ and O₂, and (2) the slow heating was determined to be caused by N₂ vibrational relaxation in air and by chemical energy release during the partial oxidation of hydrogen in the H₂–air flame.

Broadband ps-laser-based CARS measurements led the way for the removal of NRB interference in the thermometric measurements, as described above. However, the signal was still prone to collisional quenching and broadening; hence, the accuracy of thermometry was strongly dependent on accurate modeling of the collision [183]. In the meantime, with the development of fs lasers that have hundreds of cm⁻¹ available bandwidth for simultaneous excitation of the Raman transitions in multiple species, many research groups diverted their focus toward fs-CARS–based single-shot thermometric and species detection measurements [3, 153]. Most of the fs-CARS developments were focused on time-resolved rovibrational or vibrational CARS (discussed in the next subsection). Until the beginning of this century, it was believed that because of the coarse spectral resolution aided by the broadband fs probe-pulse standard fs-RCARS was not suitable for thermometry. In the early twenty-first century, Lang and Motzkus were the first to demonstrate fs-RCARS-based thermometry on CO₂ [166].

In another diagnostics development, more than three decades ago, Kaiser and co-workers had observed that with short-pulse Raman excitation and a prolonged interrogation, a narrow spectrum can be generated with high spectral resolution [178]. Recently, such a hybrid ps/fs-CARS scheme has been proposed where fs-duration pump and Stokes excite strong Raman coherence and a ps-duration probe pulse interrogates the coherence for generating CARS signal with high spectral resolution for thermometry, as demonstrated by Prince et al [176]. A hybrid-CARS scheme has the combined advantages of time-resolved spectroscopy with fs Raman excitation and frequency-resolved spectroscopy with ps-probe pulse. Slipchenko et al have demonstrated pure gas-phase thermometry using the hybrid fs/fs-RCARS scheme [177]. In the past decade, a wide range of CARS measurements have been reported with spectacular thermometry and imaging capabilities, as discussed below.

Miller et al demonstrated the first pure-RCARS employing the hybrid configuration to measure single-laser-shot gas-phase temperature measurements in a stoichiometric H₂–air flame [191]. A typical energy-level diagram and pulse sequence for hybrid RCARS is shown in figure 28. The collision-independent, NRB-free, single-laser-shot, hybrid-RCARS signal of N₂ is presented in figure 29 for various temperatures. The reported accuracies of the best-fit temperature from a probe delay of 13.5 ps exhibit accuracies of ~1% without the need of NRB or collisional corrections. J-level-dependent dephasing can also be directly measured from scanning the probe delays, while recording the CARS signal. The high spectral resolution capability of hybrid RCARS is extended to measure pressure dependence of the self-broadened S-branch linewidths of N₂ and O₂ at elevated pressures up to 20 atm [192]. From a systematic study of the RCARS of N₂ and O₂ at high pressure, it is concluded that the effect of collision can be ignored by delaying the probe up to ~6.5 ps where the thermometric errors can be maintained below 5% for pressures up to 15 atm, where, however, for pressures higher than 15 atm, the collisional effects cannot be ignored [170]. Using a time-asymmetric probe pulse for hybrid RCARS, Stauffer et al have shown that NRB-interference-free pure-RCARS can be obtained at much shorter probe delays, where the collisional dephasing is negligible; they reported single-shot accuracy (<1% error) and precision (~2.5%) for N₂ single-shot thermometry [193]. Employing a two-beam variant of hybrid fs/fs-CARS configuration [177] that allows tunability of spatial resolution by adjusting the crossing angle of the beams, Kliewer and co-workers have demonstrated single-shot 1D [194] and 2D [174, 175] RCARS thermometry, which is discussed in detail in

---

**Figure 28.** (a) Typical energy-level diagram for fs-ps-hybrid-RCARS configuration with fs pump (ω₁), Stokes (ω₂), probe (ω₃), and RCARS (ω_CARS) beams. (b) Timing sequence of overlapped pump and Stokes pulses, and time-delayed ps-probe pulse generated by a 4f pulse shaper. Reproduced with permission from [191].
section 4.6. Kearney and Scoglietti demonstrated the use of an efficient second-harmonic bandwidth compression technique, which generates a high-energy ps-probe beam that allows single-shot thermometry and \( \text{O}_2/\text{N}_2 \) ratio measurement in a flame with temperatures up to 2000 K [195]. In figure 30, the observed temperature and \( \text{O}_2 \) concentration histogram from the single-shot spectra are presented for two equivalence ratios in a near-adiabatic \( \text{H}_2-\text{air} \) flame. Another variant of the probe pulse, using two etalons has been employed to compare the accuracy and precision of hybrid fs/ps-RCARS thermometry for two probe durations (1.5 and 7 ps) [196]. Highly accurate Raman linewidth measurement of \( \text{N}_2 \) S-branch lines is demonstrated from a single-shot hybrid-RCARS configuration by splitting the probe beam into four spatially-resolved beams with independently adjustable delays; that allows simultaneous recording of the RCARS signal at four discrete probe delays [197]. A spectral-focusing-based RCARS approach has also been demonstrated, which shows bandwidth optimization of the excitation beams by introducing a delay between the pump and Stokes pulses [198]; this method is shown to be useful when chirp is present in the experiment or the laser source is not perfectly transform limited [199]. Hybrid-RCARS \( \text{N}_2 \) gas in a pressurized gas cell has been employed to measure pressures with a reported single-shot accuracy of 0.1%–6.5% [200]. Recently, a variant of ultrafast RCARS was employed to study the molecular rotation of \( \text{N}_2 \) using an optical centrifuge [201], and from the direct measurement it was shown that the dephasing of rotational lines with \( J \) value as high as \( J = 66 \) has an order-of-magnitude slower coherence-dephasing rate compared to that of low-\( J \) transitions [202].

5.2. Vibrational CARS (ps, fs, fs/ps)

As mentioned in the previous section, the rotational and vibrational temperatures can be different in nonequilibrium plasmas. The difference between the two temperatures determines the degree of nonequilibrium of the plasmas. The vibrational CARS (VCARS) spectrum is obtained by interrogating the initial population distribution of the rovibrational states (rotational manifolds across different vibrational levels) via Raman excitation. The vibrational-population distribution at a given vibrational state \( \nu \) at temperature \( T \) modifies the
general Boltzmann equation (5.1) to \[ n_v = N e^{-\hbar \omega_v / (k_B T)} \left[ 1 - e^{-\hbar \omega_v / (k_B T)} \right]. \] Since the vibrational state separations within the same electronic manifold in gas-phase molecules are much larger (e.g. \( \omega_v = \nu/c \sim 2360 \text{ cm}^{-1} \) for \( N_2 \)) than the rotational separations, only a small fraction populates the vibrational hot bands at room temperature; note that the scaling parameter in the above exponential \( \hbar / k_B = 1.44 \text{ K cm}^{-1} \). Both the low- and high-temperature regimes can be measured if rotational lines within the vibrational manifolds can be resolved. Ns-laser-based high-resolution VCARS has been routinely used in many reacting-fuel and plasma studies; however, the ns-VCARS—like in ns-RCARS, as discussed above—is plagued by significant NRB [3].

Roy et al were the first to demonstrate the ps-laser-based VCARS in the gas phase [158, 203]; this work has demonstrated three orders-of-magnitude reduction of NRB, as discussed in section 4.2. Ps-VCARS has been employed in hydrocarbon–air flames operating at different equivalence ratios; observed \( N_2 \) spectra exhibited up to three vibrational bands [204]. By temporally delaying the probe pulse in ps-VCARS, the Raman-coherence lifetimes of the rotationally resolved Q-branch transitions of \( H_2 \) have been directly measured [205]; also, the temperature has been extracted [206]. The high-speed capabilities of ps-VCARS have been significantly enhanced with the advent of the BML [72]. For example, gas-phase thermometry at a 100 kHz repetition rate has been demonstrated using ps-VCARS of \( H_2 \) in an \( H_2 \)-air flame stabilized over a Hencken burner [110]. It has also been shown that the ps duration is optimal for coupling the laser pulse into optical fibers, allowing the realization of fiber-based CARS [207]; single-shot, fiber-based ps-VCARS has also been demonstrated for measuring temperature [208]. The high-speed temperature measurement capabilities can be transitioned to highly-transient plasmas, and the fiber CARS can be implemented for harsh environments.

Montello et al have employed rotationally resolved ps-VCARS to measure the vibrational and rotational/translational temperatures in the subsonic plenum and supersonic flow of a highly nonequilibrium Mach 5 flow with a sustained discharge [209]. They have also reported the effect of the injection of \( CO_2 \), \( NO \), and \( H_2 \) in the downstream of the pulser-sustainer discharge. In figure 31, temperatures extracted from the \( N_2 \) Q-branch VCARS spectrum is presented and the flow is highly nonequilibrium with vibrational temperature three times higher than the rotational temperature. In contrast, when only 1 Torr (partial pressure) of \( CO_2 \) is injected, almost all the vibrational energy is removed from \( N_2 \), resulting in a vibrational temperature \( T_{vib} \sim 815 \text{ K} \) and a rotational/translational temperature \( T_{rot} = 630 \text{ K} \). In a point-to-plane ns streamer discharge, similar to those used in transient-plasma ignition, ps-VCARS has been employed to measure \( T_{rot} \) and \( T_{vib} \) to study the vibrational loading [210]. It was observed that the direct electron impact on vibrational excitation of \( N_2 \) is relatively inefficient in this discharge in air, but in fuel–air mixtures the electron impact accounts for nearly half of the vibrational excitation of \( N_2 \). Rapid localized heating of ns-pulse discharge has been studied employing ps-VCARS in a diffuse filament between a pair of spherical electrodes; measurements were made both in \( N_2 \) and air at 100 Torr [84]. In \( N_2 \), a temperature rise up to \( \sim 200 \text{ K} \) has been reported within \( \sim 1 \mu s \), i.e. on timescales shorter than acoustic timescales. The vibrational loading in repetitively pulsed plane-to-plane plasma has been studied employing VCARS and it is reported that up to \( \sim 50\% \) of the coupled discharge power is found to load vibrations [83].

On the fs-CARS development, after Hayden and Chandler’s first gas-phase fs-VCARS demonstration [151], many studies have been reported on fs-VCARS for gas-phase thermometry using several species, including hydrogen [159], nitrogen [165], etc. Unlike ps-VCARS, since fs-VCARS is inherently collision independent, the fs-VCARS signal of \( N_2 \) could be obtained for pressures up to 5 bar and used for studying collision-induced rotational-energy transfer rates [167, 169]. Time-resolved fs-VCARS was also employed for high-temperature thermometry in a \( H_2 \)-air diffusion flame, where the decay rate of the initial Raman coherence was used as a measure of temperature [155]. Since at different temperatures a different number of rovibrational levels are excited, the collective CARS signal obtained from those levels dephases at different rates; the collective dephasing has been named ‘frequency-spread dephasing’ (FSD) [154, 168]. Measuring those decay rates from time-resolved VCARS yields the temperature of the target \( N_2 \) gas. Furthermore, the broadband fs lasers (bandwidth \( \sim 350 \text{ cm}^{-1} \) for 100 fs pulse) can simultaneously excite multiple molecules at the target volume; Roy et al have investigated the polarization beating of \( N_2 \) in the presence of \( CO \) in the FSD-based fs-VCARS thermometry [156]. It has been reported that the presence of \( CO \) does not impact the accuracy of \( N_2 \)-based thermometric measurement, particularly for the \( CO \) concentrations present in typical reacting flows. Furthermore, the depth of the modulation produced from polarization beating could be used for extracting other major species with concentration \( > 5\% \). Similarly, the presence of \( CO_2 \) on \( O_2 \) fs-VCARS thermometry has also been investigated in a heated cell and it has been
observed that the thermometric measurement is affected when CO\textsubscript{2} concentration reaches over 10%; it is concluded that careful modeling of fs-CARS is required to achieve the thermometric accuracy for such mixtures [211]. Bitter and Milner have presented another strategy for single-shot measurement of species concentration by separating the VCARS signals from a mixture of O\textsubscript{2} and CO\textsubscript{2} by exploiting a ‘silence window’ of one of the species in time domain [212]. The collisional effects on N\textsubscript{2} fs-VCARS is studied at high pressures (up to 50 bars) in the presence of different collisional partners [46], as discussed earlier in section 4.4.

It has been shown that the thermometric information from N\textsubscript{2} VCARS can be extracted by mapping the FSD of the Raman coherence using a chirped-probe pulse [86], as discussed earlier in figure 24. The measurement accuracy and precision for measuring a temperature range of 300–2400 K in a near-adiabatic laboratory flame is found to be \( \sim 1\%–6\% \) and \( \sim 1.5\%–3\% \), respectively. This method is applied to extract the temperature from a driven flame at 1 kHz-data-acquisition rate [171]. A detailed model for the chirped-probe fs-CARS is developed, and the results are compared with the experiment; also, it is reported that the mean temperature accuracy is within \( \sim 3\% \) with respect to the adiabatic flame temperature [213]. Chirp-probe fs-VCARS is also used to measure species concentrations in gas mixtures of CO–N\textsubscript{2} and Ar–N\textsubscript{2} at atmospheric pressure [214].

Furthermore, to selectively measure species in a mixture of multiple molecules, a spectral-focusing method was employed by Wrzesinski et al [198]. In this approach, the broadband fs pump and Stokes pulses were chirped and delayed with respect to each other, which allowed the pump and Stokes pair to selectively and controllably excite the Raman transition of one of the molecules. In a 10-bar, 1:1 binary mixture of O\textsubscript{2} and CO\textsubscript{2}, selective excitation of each of these species was demonstrated by varying the delay between the pump and Stokes pulse. Keeping the delay of the pump and Stokes pulse fixed, the coherence dephasing of either of the species was measured from the time-resolved VCARS signal using a delayed probe without interference from other species.

The hybrid fs/ps-CARS approach (described earlier in section 5.1) is also employed for spectrally-resolved VCARS of N\textsubscript{2} [215]. Using a pulsed high-temperature flame, high-speed real-time N\textsubscript{2} thermometry is demonstrated, as shown in figure 32. The narrowband time-asymmetric ps-duration probe is prepared using a 4f pulse shaper and filters; using such a probe hybrid, VCARS of N\textsubscript{2} is measured in a H\textsubscript{2}-air stabilized over a Hencken flame and it is concluded that using a sharply raised pulse excites the FSD of the Raman coherence to be zero—eliminating the need for correction procedures [216]. Enhanced sensitivity of flame thermometry has been reported employing hybrid VCARS of N\textsubscript{2} for a temperature range 300–2400 K [217]. Hybrid VCARS has also been used to measure the mole fraction of CH\textsubscript{4} in a gas binary mixture with N\textsubscript{2} [218]. Scherman et al have achieved a high spectral resolution of \( \sim 0.7 \text{ cm}^{-1} \) in the hybrid-VCARS measurement of N\textsubscript{2} using a fiber-based fs-laser and deriving the ps probe from the fs beam using a volume Bragg grating [219]. Stauffer et al have presented a detailed theoretical and computational analysis of hybrid VCARS with time- and frequency-domain models for both gas-phase thermometry and condensed-phase excited-state dynamics to show the robustness in quantitative analysis using various probe-pulse shapes [220]. Marrocco has presented theoretical analysis of the effects of different pulse shapes in hybrid CARS [221]; also, analytical results for different pulse shapes are presented [222].

In a recent study, the chirped-probe CARS and hybrid-VCARS methods are compared for temperature measurement in near-adiabatic flames [223]. It is reported that chirped-probe CARS requires more optimization of model parameters to extract the temperature compared to the hybrid VCARS, and hence the computational cost is significantly less for the hybrid-CARS configuration. Another variant of hybrid ps/fs-VCARS has been reported, where both pump and probe are ps-duration pulses and Stokes is a broadband fs pulse, for observing both time and frequency-resolved CARS spectra of various C-H stretch regions in condensed-phase molecules [224, 225]. Hybrid CARS and other VCARS configurations have also been used in completely different applications, e.g. for the standoff detection of bacterial spores [226–229], and in high-wavenumber regimes in liquids [230–232].

5.3. Broadband CARS (single-beam fs, dual-pump fs/ps, ultrabroadband fs/ps)

The availability of ultrashort lasers, with their durations shorter than the typical molecular vibrational period and bandwidths of a few thousand cm\textsuperscript{-1}, has enabled single-beam VCARS spectroscopy for microscopic and standoff detections [233–236]. Typical broadband fs-duration lasers provide sufficient bandwidth (\( \sim 200–300 \text{ cm}^{-1} \)), with corresponding transform-limited durations (50–70 fs) to access low-frequency Raman modes (0–600 cm\textsuperscript{-1}) via impulsive excitation. However, frequency-conversion approaches have been
developed that allowed the formation of ultra-broadband ultra-fast pulses with bandwidths of the order of a few thousand cm$^{-1}$. Employing phase and polarization shaping of broadband continuum of ultrashort pulses of duration $\sim$7 fs with a spectral bandwidth of $\sim$3500 cm$^{-1}$, as introduced by Silberberg and co-workers [237], Roy et al. have shown how a broadband pump and Stokes and a narrowband probe beam present in the single beam can be utilized for N$_2$ CARS spectroscopy [238]; the spectra of the three beams and the generated CARS signal are shown in figure 33. This single-beam configuration has also been employed for the simultaneous excitation of CO$_2$ Fermi dyads at $\sim$1285 and $\sim$1388 cm$^{-1}$, and the variation of CARS signal intensities for the two lines under different pressure conditions have been analyzed and the concentration of CO$_2$ is measured in a mixture of CO$_2$–Ar in a cell [239]. Single-shot N$_2$ thermometry is demonstrated employing a single-beam configuration with three different delayed probes using glass cover slips to measure the Raman depoling and extract temperature from a depoling-temperature calibration [240].

Bohlin and Kliewer demonstrated the utilization of the ultra-broadband spectrum of 3500 cm$^{-1}$ associated with a 7 fs pulse in a hybrid-CARS configuration—which is also called as multiplex CARS—to acquire the RCARS and VCARS data simultaneously from multiple gas-phase species, such as N$_2$, H$_2$, CO$_2$, O$_2$, and CH$_4$ [241]. The spectrally-resolved, broadband, multiplexed VCARS of a few species obtained from a two-beam configuration is presented in figure 34. The same group extended the ultra-broadband multiplex CARS to obtain simultaneous single-shot rotational and vibrational CARS of H$_2$ [242]. Covering a spectral region spanning 4200 cm$^{-1}$, they have demonstrated planar thermometric measurements with high spectral and spatial resolution in a H$_2$-diffusion flame. This approach has further been employed to obtain simultaneous CARS imaging and broadband chemical detection in a fuel-rich premixed hydrocarbon flat flame (ethylene/air $\Phi = 2.35$) [243]. The authors of the work have demonstrated robust 1D-CARS thermometry from the spectrally-resolved rotational S-branch transitions of N$_2$ for a temperature range of 300–1600 K.

5.4. Simultaneous measurements of vibrational and rotational temperatures for the characterization of nonequilibrium environments

The high-speed, spatially-resolved, multidimensional, single-shot CARS capability for the simultaneous measurement of vibrational and rotational temperatures, as discussed in the previous subsections, would be extremely useful for highly-transient plasmas to understand the degree of nonequilibrium in plasmas and the process of energy transfer to vibrational and rotational/translational states of the plasmas (also discussed in section 5.2). In the highly-transient nonequilibrium plasmas, high-spatial and -temporal resolution thermometry and species-concentration measurement are critical for getting quantitative insight into the plasma kinetics, as discussed earlier in sections 2.2 and 2.3. Montello et al. have employed ps-CARS to obtain the nitrogen Q-branch spectrum in a nonequilibrium subsonic plenum and supersonic wind tunnel excited by a ns pulser/DC sustainer electric discharge with enhanced spatial resolution [209]; the rotational/translational and vibrational temperature are derived from the rotationally resolved N$_2$ VCARS spectrum. It is concluded that while the pulsed-discharge results in significant vibrational loading, the rise in rotational/translational temperature remains nominal. Transient-plasma ignition conditions are evaluated by measuring the N$_2$ vibrational CARS in a discharge afterglow in C$_2$H$_4$/air, CH$_4$/air, and C$_3$H$_8$/air mixtures; this measurement allows for the determination of the temporal evolution of rotational and vibrational temperatures [210]. The vibrational energy loading and relaxation kinetics of N$_2$ in a pulsed nonequilibrium plasma in both pin-to-pin and plane-to-plane geometry have been studied using ps-VCARS, and rotational/translational temperature is extracted from the rotationally resolved signal [83]. In a plasma-assisted combustion, simultaneous LIF of intermediate species OH and ps-VCARS-based vibrational and rotational thermometry has been presented [244]. Note that all of the simultaneous measurements of the rotational and vibrational temperature are derived from spectrally-resolved VCARS only.

Although ps-CARS can provide sufficient resolution to measure rotational and vibrational temperature simultaneously, such measurements are limited to low repetition rates, as discussed earlier. Extending the ps-CARS measurements to fs-laser-based measurements, all of the broadband advantages for Raman excitations are realized. Employing fs/ps-hybrid CARS, simultaneous rotational and vibrational CARS of multiple species (N$_2$, O$_2$, CH$_4$, H$_2$), mole fractions of the combustion species has been measured simultaneously [245]. Dedic et al. have measured N$_2$ vibrational and rotational temperature in a ns-laser-induced spark generated in a nitrogen jet [246]; and they have shown that the rotational temperature varies from 540–542 K, and the vibrational temperature varies from 1100–1600 K when the measurement time was delayed between 2–5 $\mu$s after the shock. The simultaneous measurement of RCARS and VCARS in an ns-laser spark of N$_2$ jet are
reported; also, the shadowgraph of the shock wave is recorded [247]. Many rotational lines and vibrational hot bands in the CARS spectra are reported to appear for longer measurement delays after the laser-induced shock, which demonstrated the increase in both rotational and vibrational temperature, particularly after 1.1 μs. However, the signal is reported to decline after 2 μs primarily because of the expansion of the plasma kernel. The dual-pump ps/fs-hybrid CARS has been employed in a detonation environment to measure simultaneously the vibrational and rotational temperature on a shot-to-shot basis [248]. Dedic, Meyer and Michael have demonstrated single-shot rotational and vibrational temperature in a DBD plasma using the hybrid-CARS signal from S- and Q-branch of N2, as shown in figure 35 [249]. The authors have reported that because of the high concentration of N2, the plasma was unsteady and the location of the large filament structure was changing with time. Clearly, the rotational/translational temperature almost remains invariant, whereas the vibrational loading is found to differ significantly from shot to shot. These measurements in the nonequilibrium plasma are achieved with a spatial resolution of ~650 μm and a sampling rate of <10 ps. This work outlines the potential of linear or planar measurements at higher repetition rates in plasma environments.

6. Prospects for collision-free measurements of other chemical species

CARS has long been used as a preferred approach for gas-phase thermometry, but it is typically limited to major flame or plasma species (such as N2 and O2), because the CARS signal intensity is proportional to the square of the number density of the target species. Hence, the SNR is low for the detection of minor species [43]. Since minor species also play an important role in spatial, temporal, and chemical dynamics in a reactive environment, it is important to develop suitable detection techniques. A variant of CARS known as ERE-CARS (briefly discussed in section 4.3), where the probe couples resonantly to the electronic transition in the measured species, has been demonstrated using ns-duration lasers to

![Figure 34](image_url)

Figure 34. Multiplex CARS with high spectral resolution measurement of vibrational manifold for four different species (a) CH4, (b) N2, (c) CO2 Q-branch, and (d) CO2 S-branch. Experimental setup was the same for all of the experiments. Reprinted with permission from [241]. Copyright (2014), AIP Publishing LLC.

![Figure 35](image_url)

Figure 35. (a) Histogram of the extracted single-shot vibrational temperature $T_{\text{vib}}$ and rotational temperature $T_{\text{rot}}$ measured at the center of the DBD. Pair of single-shot spectra plotted in (b) and (c) with the corresponding best-fit temperatures $T_{\text{rot}} = 380$ K, $T_{\text{vib}} = 2850$ K, respectively; similarly (d) and (e) correspond to $T_{\text{rot}} = 390$ K, and $T_{\text{vib}} = 3460$ K, respectively. Reproduced with permission from [249].
enhance the CARS signal by a few orders-of-magnitude and, hence, is suitable for the detection of minor species such as NO [250]. Even with the use of pulses longer than quenching timescale, ERE-CARS has been demonstrated to be quenching independent [251]. In ERE-CARS, the simultaneous exploitation of both vibrational and electronic resonances during the three-color excitation process results in a high degree of chemical specificity, allowing for detection that is free of interference from other species with similar electronic transitions [252]. From careful theoretical analysis it was demonstrated that ERE-CARS is dependent on the coherence-dephasing rate but independent of the electronic quenching rate, and such dephasing dependence can be overcome by operating near the saturation condition for probe coupling [163, 253]. The saturation conditions for the probe pulse in ERE-CARS have been analyzed theoretically for pulse durations ranging from ns to fs [164]. It is observed that for pulse durations longer that collisional timescales, the threshold intensity for saturation is independent of the duration of the pulse; however, for pulse durations shorter than collisional timescales, the threshold intensity of saturation is inversely proportional to the square of the pulse duration. The advantage of electronic resonance was also realized in other configurations, such as three-photon resonant CARS [254] and degenerate four-wave mixing (DFWM) [43].

In spite of these advantages associated with the electronic resonances, these techniques are typically limited to frequency-domain approaches that exploit ns-duration laser pulses; also this technique is often limited to acquisition rates of ~10 Hz based on the repetition rates of the high pulse energy ns lasers.

6.1. FREE-CARS for minor-species detection

Recently, Stauffer et al demonstrated an fs-laser-based, non-invasive optical approach that allows simultaneous gas-phase thermometry and minor-species-concentration measurements under single-laser-shot conditions [255]. In this approach, referred to as FREE-CARS, two independently tunable, UV pulses are employed to induce resonant coupling of electronic transitions of minor species. The FREE-CARS approach provides highly sensitive, spectrally-resolved signature of multiple rovibrionic transitions of minor combustion species (OH, NO). This technique allows for the simultaneous access to molecular transitions spanning 200–300 cm\(^{-1}\) (an approximately ten-fold increase over prior DFWM approaches) at acquisition rates of 1 kHz (100-fold increase). Implementation of the broadband fs-duration pulses in FREE-CARS also allows simultaneous temperature and species-concentration measurements that are quenching independent [96]. The versatility of fs-duration laser pulses also allows easy access to multiple tunable pulses that cover a broad range of wavelengths; thus, these approaches can exploit multiple electronic resonances to increase detection sensitivity dramatically. The experimental setup used for the FREE-CARS measurement is shown in figure 36(a). With the ability to scan the timing between the pulses (as shown in figure 36(b)), many rovibrational states in the ground and excited electronic states can be mapped. The resonant coupling of the two UV lasers in the FREE-CARS configuration and the diagram associated with the most significant FWM term. Reproduced with permission from [96].

Spectrally and temporally resolved FREE-CARS signal of NO acquired from a mixture of NO with Ar is plotted in figure 37; figure 37(a) is the contour plot of the FREE-CARS signal; figure 37(b) is the typical time-resolved FREE-CARS signal obtained by integrating over the spectrum; figure 37(c) is the spectrally-resolved signal obtained by integrating the signal over the whole range of the delay \(\tau_{23}\) [255]. All of these data were taken with the pump-Stokes delay \(\tau_{23}\) fixed at 500 fs. While the electronic dephasing is likely responsible for the observed decay of the signal, the high spectral resolution is afforded by the signal integration over the electronic dephasing time of several ps.

The high-resolution measurement capability of this technique has been employed to determine simultaneously the temperature and number density of OH from single-laser-shot FREE-CARS in a laminar flame, as shown in figure 38 [96]. The highly sensitive single-shot temperature data were obtained with excellent temperature accuracy (2.2% compared to adiabatic flame temperature) and precision (average 2% standard deviation) and compared very well with previous results [215]. Similarly, the accuracy and precision of the number-density measurements are reported to be reasonable, with high detection sensitivities (100–300 ppm) at flame temperature.

Molecular wavepacket dynamics and their control has been demonstrated employing fs lasers resonant to molecular transitions in various diatomic molecules employing pump-probe configurations [256–259].
6.2. Other FWM techniques

Many FWM techniques have been extensively used for gas-phase diagnostics [43] and in plasmas [53, 56]. In a recent work, an fs time-resolved parametric FWM (fs-PFWM) technique is developed [260]. In PFWM, a molecular electronic state is excited by a resonant two-photon transition using an fs-laser, which is followed by a second fs-duration probe pulse (ω2) inducing the coherent and directed outgoing signal pulse (ωPFWM), allowing much faster measurements to be made compared to the fluorescence lifetime. Note that the excitation scheme of PFWM is similar to TALIF, but unlike TALIF that generates signal in all $4\pi$ steradian, the PFWM signal is directed because of the coherent probing of the two-photon coherence. By precisely scanning the temporal delay between pulses 1 and 2, the time-dependent spectral signature of the two-photon-excited species can be mapped using this approach. Figure 39, for example, depicts the fs-PFWM signal observed for nitric oxide (NO) gas in the presence of N2 and CO2 bath gases. Inset: Calculated room-temperature Boltzmann-weighted NO TPA spectrum. Squared-magnitude of pump-pulse intensity pro included for reference. [260] John Wiley & Sons (Copyright © 2016 John Wiley & Sons, Ltd).

Figure 38. Single-shot OH spectra (solid curves) plotted for different equivalence ratios (a) $\phi = 0.45$, (b) $\phi = 1.0$. Simulated spectra (dashed) and residual (brown line offset for clarity) are shown. In the inset, histograms of the best-fit temperature for 1000 laser shots are shown. Reproduced with permission from [96].
two-photon-absorption cross-sections from ground-state NO, assuming a room-temperature Boltzmann distribution of the initial states.

Although all of the resonant nonlinear techniques discussed in this section have been realized for mixtures in gas cells or reacting flows, they can be easily extended to measure minor species in reacting plasmas too. These techniques will be particularly useful for measuring the time-resolved species concentration of reaction intermediates in plasmas, e.g. NO, OH, etc., that are crucial to understanding the kinetics.

7. Concluding remarks and future opportunities

We have reviewed the rapid growth and advances in the development of ultrafast-laser-based spectroscopy and imaging for reacting plasmas and flames over the past two decades. We have discussed spectroscopic measurements with expanded capabilities for obtaining spatially and temporally resolved measurements of the key performance parameters related to highly-transient reacting flows such as temperature, number densities of atomic and molecular species, electric fields, and velocimetry. With orders-of-magnitude higher intensities compared to traditional ns lasers, ultrashort-pulse lasers have enabled 1D and 2D single-shot measurements at repetition rates of 1 kHz or higher, which was unthinkable only a few years ago. We have also reviewed the use of fs-laser-based measurements for circumventing various interferences in spectroscopic approaches that are common in ns-laser-based measurements. We have discussed the ability of these new measurement techniques to enable detailed understanding of plasmas and flows and aid the development of predictive models for reacting plasmas and flames.

Highly-transient and nonequilibrium plasmas have been widespread in many plasma applications in a variety of configurations such as DBDs, pin-to-pin discharges, and plasma jets sustained by AC, DC, or short (ns) electrical pulses. However, until recently, plasma characterization has mainly employed long-duration ns lasers, which severely limited capabilities in terms of the quantitative understanding of plasmas. We have discussed in detail the current state-of-the-art plasma diagnostics for electric-field measurements using both linear (such as emission spectroscopy) and nonlinear (such as FWM, SHG, and CARS) methods, electron temperature and density measurements (using Thomson scattering), thermometry (using CARS), number density of atomic species such as H, O, and N atoms and radical species such as OH and NO (using LIF and PLIF). The technical challenges and future prospects have been outlined for each of these measurements.

Although ns-laser-pumped LIF and PLIF measurements have been extremely useful in measuring minor species with very high sensitivity, they have not been suitable for measuring higher concentrations of intermediate atomic and molecular species, because of large absorptions. With TALIF measurements, the two-photon excitation of atomic species with UV beams has reduced absorption during the propagation, but since the nonlinear process is intensity dependent, a much higher fluence has been required to obtain the ns-TALIF signal. The higher fluence causes photolytic dissociation of other molecules, which has resulted in extremely large photolytic interference in the signal. In contrast, the excitation of atomic and molecular species with short-duration pulses has essentially eliminated the photolytic dissociation. It has been shown that the fs-laser with its high intensity and ultrashort-duration efficiently excites the measured species, and the TALIF signal has been generated without photolytic interferences. The comparison of ns-TALIF and fs-TALIF has been discussed and recent advancements in accurate fs-TALIF measurements of key intermediates such as H and O atoms and reactive radicals OH and NO, along with the single-shot and 2D measurement capabilities have been reviewed.

For thermometric measurements in reacting plasmas and flames, ns-CARS has been the most popular nonintrusive technique. However, ns-CARS has suffered from the following drawbacks: the signal, accompanied by strong NRB, has limited the accuracy and sensitivity; also the thermometric accuracy has been strongly dependent on the collisional models, which limited its usefulness to steady flows with known collisional environments. In this review, we have discussed the impact of fs lasers in fueling the developments in ultrafast CARS research with many advanced capabilities that were unthinkable only a few years ago. Very rapid growth has taken place over the past two decades in fs-CARS-based thermometry and species-concentration measurement capabilities, including: (a) NRB-interference-free measurements, (b) time-resolved single-shot measurements with kilohertz or higher repetition rate, (c) spatially-resolved measurements, (d) 1D and 2D measurements, and (e) simultaneous measurements of multiple species. The paths to realization of each of these capabilities have been extensively reviewed. Also, we have discussed the new avenues that have opened up with these capabilities, such as time-resolved measurements at high pressure (50 bar or higher) afforded by collision-independent fs-CARS and thermometry using fiber-coupled CARS in harsh environments.

Many different configurations that have been employed for fs-CARS-based interference-free and collision-independent gas-phase thermometry and species-concentration measurements in the literature have been extensively discussed. Myriad recent developments in rotational- and vibrational-temperature measurements employing ps lasers, chirped fs pulses, spectral focusing, single-beam, and hybrid fs/ps-CARS have been reviewed both for temporally and spectrally-resolved detections. These developments have been reported ranging from equilibrium to highly nonequilibrium conditions with test targets such as gas cells, gas jets, adiabatic and turbulent flames, hypersonic environments, high-pressure plasmas and flames. The ultra-high bandwidth (∼3500 cm⁻¹) afforded by ultrashort, 7 fs pulses has allowed the realization of single-beam CARS thermometry and simultaneous multiple species measurements (N₂, H₂, O₂, CH₄, CO₂, etc). Simultaneous 2D single-shot, temperature and concentration measurements have significantly increased the prospect of employing fs-CARS tools for understanding...
combustion mechanisms in turbulent flows and practical combustors. For highly-transient nonequilibrium plasmas, the rotational/translational temperature can be very different from the vibrational temperature, and the degree of nonequilibrium dictates the plasma kinetics. Hence, simultaneous measurement of rotational and vibrational temperatures with high temporal and spatial resolution has been critical to understanding energy transfers and complex plasma kinetics; such measurements will help in validating the plasma models. A few recent studies from the literature have been discussed where simultaneous measurements of the rotational and vibrational CARS signal in nonequilibrium plasmas were performed to obtain single-shot rotational/translational and vibrational temperatures. A few resonant variants of CARS and FWM have been presented, which would be suitable for time-resolved concentration measurement of reaction intermediates in the plasmas.

7.1. Future opportunities

Fs-TALIF can be useful for measuring many other chemical species and reaction intermediates. While fs-TALIF excitation is inherently collision independent, the measurement time limits the capability of this technique for obtaining the time-resolved fluorescence signal. Advanced gated detection with gate duration shorter than the quenching timescale could aid the direct measurement of the quenching rates in transient conditions. Such gated detection may be helpful for making measurements in high-pressure conditions to obtain scaling laws of the reaction intermediates. With the availability of the high-repetition rate (kilohertz to megahertz) high-power lasers, TALIF measurements may be extended to volumetric measurements. Such high-dimensional measurements could aid in the capture of the complete dynamics associated with turbulent flows; e.g. in highly-transient plasmas or in high-pressure plasma conditions. Many future opportunities exist for fast, interference-free, higher-dimensional ultrafast diagnostics of plasmas using CARS, FWM, etc. These ultrafast diagnostics could be able to perform plasma characterization and imaging in extreme conditions such as those under the Sun-like extreme mix of temperature (hundreds of millions of Kelvin), pressure (hundreds of millibars to gigabars), and number density; direct measurement of these parameters would be critical for the realization of self-sustainable fusion ignition in a controllable way for extracting useful energy.

Acknowledgments

We gratefully acknowledge a host of outstanding colleagues and collaborators with whom we have interacted over the course of the past decade in the area of TALIF and CARS spectroscopy. Their tremendous expertise and enthusiasm have contributed immeasurably to many of the efforts described in this review. Of particular note are the contributions of late Prof Walter Lempert, Prof Terrence Meyer, Dr Hans Stauffer, Dr Paul Hsu, Dr Naibo Jiang, Dr Paul Wrzesinski, Dr Joseph Miller, Dr Daniel Richardson, Dr Benjamin Hall and Dr Jake Schmidt. Special thanks to Dr Hans Stauffer for thorough and detailed proof reading of the manuscript and excellent discussions on ultrafast CARS, and to Dr Naibo Jiang for helpful discussions on plasma diagnostics. The authors gratefully acknowledge the funding provided by the Air Force Research Laboratory under Contract Nos. FA8650-15-D-2518, by the Air Force Office of Scientific Research (Dr Enrique Parra and Dr Chiping Li, Program Officers), and the editorial assistance provided by Ms Marian Whitaker.

References

[11] Benard N and Moreau E 2014 Electrical and mechanical characteristics of surface AC dielectric barrier discharge plasma actuators applied to airflow control Exp. Fluids 55 43
[13] Leonov S B, Adamovich I V and Soloviev V R 2016 Dynamics of near-surface electric discharges and mechanisms of their interaction with the airflow Plasma Sources Sci. Technol. 25 063001
[22] Höft H, Becker M M, Loffhagen D and Kettlitz M 2016 On the influence of high voltage slope steepness on breakdown and development of pulsed dielectric barrier discharge Plasma Sources Sci. Technol. 25 064002
[23] Stepanyan S A, Starikovskiy A Y, Popov N A and Starikovskaya S M 2014 A nanosecond surface dielectric barrier discharge in air at high pressures and different polarities of applied fields: transition to filamentary mode Plasma Sources Sci. Technol. 23 045003
[28] Eckbreth A C 1996 Laser Diagnostics for Combustion Temperature and Species (Amsterdam: Gordon and Breach)
[35] Schmidt J and Ganguly B 2013 Effect of pulsed, sub-breakdown applied electric field on propane/air flame through simultaneous OH/acetonitrile LIF FLAME. 160 2820–6
[50] Hoder T, Loffhagen D, Vorec J, Becker M M and Brandenburg R 2016 Analysis of the electric field development and the relaxation of electron velocity distribution function for nanosecond breakdown in air Plasma Sources Sci. Technol. 25 15
[90] Verreycken T and Bruggeman P J 2014 OH density measurements in nanosecond pulsed discharges in atmospheric pressure N₂–H₂O mixtures Plasma Sources Sci. Technol. 23 015009


[98] Hansch T W 1977 High-resolution spectroscopy of atoms and molecules Phys. Today. 30 34


Ono R, Takezawa K and Oda T 2009 Two-photon absorption laser-induced fluorescence of atomic oxygen in the afterglow of pulsed positive corona discharge J. Appl. Phys. 106 043302


Bowman S S, Adamovich I V and Lempert W R 2014 Experimental and modeling analysis of singlet delta oxygen kinetics in a repetitively pulsed nanosecond discharge Plasma Sources Sci. Technol. 23 035009


Teramoto Y, Ono R and Oda T 2012 Production mechanism of atomic nitrogen in atmospheric pressure pulsed corona discharge measured using two-photon absorption laser-induced fluorescence J. Appl. Phys. 111 113302


Verreycken T, Mensink R, Horst R V D, Sadeghi N and Bruggeman P J 2013 Absolute OH density measurements in the effluent of a cold atmospheric-pressure Ar-H2O RF plasma jet in air Plasma Sources Sci. Technol. 22 055014


Zheltikov A M 2000 Coherent anti-stokes Raman scattering: from proof-of-the-principle experiments to femtosecond CARs and higher order wave-mixing generalizations J. Raman Spectrosc. 31 653–67


resolution in vibrational imaging via saturated coherent anti-Stokes Raman scattering. Phys. Rev. Appl. 4 014010


[245] Dedic C E, Miller J D, Meyer T R and Gord J R 2013 51st AIAA Aerospace Sciences Meeting (Dallas, TX)

[246] Dedic C E, Michael J B and Meyer T R 2015 15th AIAA Aviation Technology, Integration, and Operations Conf. (Dallas, TX)


[248] Dedic C E, Michael J B and Meyer T R 2017 Investigation of energy distributions behind a microscale gas-phase detonation tube using hybrid fs/ps coherent anti-Stokes Raman scattering 55th AIAA Aerospace Sciences Meeting (Grapevine, TX) (ARC) 2017-0030


