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Single-shot gas-phase thermometry using pure-rotational hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering

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Abstract: High-repetition-rate, single-laser-shot measurements are important for the investigation of unsteady flows where temperature and species concentrations can vary significantly. Here, we demonstrate single-shot, pure-rotational, hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering (fs/ps RCARS) thermometry based on a kHz-rate fs laser source. Interferences that can affect nanosecond (ns) and ps CARS, such as nonresonant background and collisional dephasing, are eliminated by selecting an appropriate time delay between the 100-fs pump/Stokes pulses and the pulse-shaped 8.4-ps probe. A time- and frequency-domain theoretical model is introduced to account for rotational-level dependent collisional dephasing and indicates that the optimal probe-pulse time delay is 13.5 ps to 30 ps. This time delay allows for uncorrected best-fit N2-RCARS temperature measurements with ~1% accuracy. Hence, the hybrid fs/ps RCARS approach can be performed with kHz-rate laser sources while avoiding corrections that can be difficult to predict in unsteady flows.

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1. Introduction

Coherent anti-Stokes Raman scattering (CARS) spectroscopy has found significant use in the measurement of gas-phase temperature and species concentration due to its ability to probe harsh environments and provide high spatio-temporal resolution in unsteady flows [1–3]. This technique utilizes a pump beam with frequency $\omega_1$ and Stokes beam with frequency $\omega_2$ to excite rotational or vibrational Raman resonances ($\omega_1 - \omega_2$) in a molecule. A probe pulse ($\omega_3$) is then used to generate a coherent anti-Stokes signal ($\omega_1 - \omega_2 + \omega_3$) with a spectral fingerprint that is sensitive, in part, to temperature and species concentration. Excitation of high-energy vibrational resonances is often utilized for thermometry in combusting flows up to 3500 K [1]. In low-temperature unsteady flows, where physical probes would be ineffective, it is possible to excite well isolated hydrogen ro-vibrational transitions down to 300 K [4] or, more commonly, low-energy pure-rotational transitions of species such as oxygen and nitrogen. Examples of the latter include studies in turbulent boundary layers from 300 to 500 K [5] and pre-ignition in internal combustion engines from 400 to 700 K [6]. Other low-temperature applications that may benefit from the sensitivity of the rotational CARS technique include pyrolysis reactors from 600 to 800 K [7], biomass pretreatment systems from 500 to 600 K [8], and catalytic reformers from 400 to 700 K [9].

Unfortunately, high-power nanosecond (ns) laser sources required for single-shot detection are limited to ~10-30 Hz, a rate that is incapable of resolving the time-history of temperature or species concentrations in most unsteady flows. While offering excellent spectral resolution for measuring multiple molecular species and temperature [4,10], ns-CARS signals are also subject to interferences from nonresonant background [11] and molecular collisions [12] that can vary with temperature, density, and chemical composition. This is a source of uncertainty for single-shot measurements in unsteady flows.

Several developments in CARS spectroscopy in recent years have focused on alleviating these weaknesses. For example, picosecond (ps) CARS with ~100-ps pulses has been introduced to suppress nonresonant background [13–19]. This is achieved by temporally separating the probe pulse from the pump and Stokes preparation pulses during the sub-ns coherence lifetime of the Raman resonance. This allows nonresonant background suppression by three orders of magnitude while maintaining excellent CARS signal levels and spectral resolution for frequency-domain detection and analysis [13–19]. A potential weakness of this approach is that probe delays in excess of 100 ps are required to suppress nonresonant interferences, which allows sufficient time for the spectra to become sensitive to collisional energy transfer, especially at lower temperature [17–19]. These effects create an apparent shift in temperature due to rotational-level-dependent dephasing rates [17–19], which may be difficult to model in unsteady flows with time-varying species concentrations. In addition to sensitivity to collisions, high-power ps lasers for single-shot detection have low repetition rates (~10–30 Hz) similar to that of ns lasers.

In contrast to the high spectral resolution of ns- and ps-CARS systems, time-domain CARS signals can be acquired using kHz-rate ultrafast lasers with pulse widths on the order
of 100 fs. Instead of frequency-domain detection of the molecular distribution, the time-dependent molecular response is resolved by temporally delaying the CARS probe from the initial Raman resonance induced by the pump and Stokes pulses [1,20–26]. By utilizing the slope of the initial decay of the CARS signal due to frequency-spread dephasing, it is possible to extract gas-phase temperatures without interferences from collisional energy transfer [23-26]. Initial measurements utilized a slow-scan mechanical delay stage to probe the ro-vibrational Raman coherence at various time delays relative to the initial impulsive excitation [23,24]. Subsequent efforts employed a chirped probe pulse to instantaneously encode the time decay into the spectral domain for single-shot, time-domain thermometry using a spectrometer [25]. However, this approach is highly sensitive to the probe pulse shape and phase, which should be characterized in great detail for accurate measurements. Hence, spectral modeling for single-shot, chirped-probe fs CARS thermometry can be complicated by several factors, including nonresonant interferences (used to increase signal strength) [25], interferences from resonant modes of multiple species [26], and the presence of density gradients or test cell windows that may alter the characteristics of the probe pulse. Current research is attempting to address these challenges using advanced pulse shaping, calibration, and characterization techniques [27]. For pure rotational spectra, however, the complexity can increase significantly because many molecules are probed simultaneously [17].

In an effort to exploit the advantages of both time- and frequency-resolved spectroscopy and utilize the high (kHz) repetition rate of ultrafast amplifiers, Miller et al. [28] have investigated the use of hybrid fs/ps CARS for gas-phase thermometry. By using 100-fs pulses to excite multiple molecular transitions and then probing the molecular response in the frequency domain using a 1-10 ps probe pulse, nonresonant and collisional interferences can be avoided through time-delayed detection. However, sufficient spectral resolution is maintained in the transform-limited, ps probe pulse for detection of multiple species with much reduced sensitivity to probe-pulse characteristics [29]. In the case of vibrational hybrid fs/ps CARS, the temperature sensitivity is derived from the relative ratio of the fundamental and first-excited vibrational transitions [28]. As a result, the technique is only sensitive at temperatures where there is appreciable population in the excited vibrational states, thus limiting the technique to ~1200 K and higher [1]. In contrast, rotational CARS derives its temperature sensitivity from the distribution of rotational energy states, primarily in the ground vibrational state, which are active even at very low temperatures near 300 K [17]. In addition, rotational CARS can potentially be used to detect multiple species due to the broadband nature of the fs pump and Stokes pulses.

Therefore, the primary goal of the current work is to demonstrate the first use of single-laser-shot, hybrid fs/ps, pure-rotational CARS (fs/ps RCARS) for spectrally-resolved, collision- and nonresonant-background-free measurements of gas-phase temperature. Single-shot signal-to-noise ratios (SNR) of RCARS spectra are evaluated from 300 to 800 K using individual pulses from a kHz-rate fs laser amplifier. This approach has the potential to provide accurate kHz-rate thermometry with reduced sensitivity to probe-pulse characteristics at temperatures that are lower than that accessible using vibrational fs/ps CARS. We also present, to our knowledge, the first demonstration and validation of a time- and frequency-resolved fs/ps RCARS model to account for rotational (J-level) dependent dephasing, as called for in the literature [18,19]. Diatomic nitrogen is used as a sample molecule due to its abundance in air-breathing reactions and its wide use in gas-phase CARS thermometry. Direct measurement of J-level dependent collisional dephasing of N\textsubscript{2} in the range 13.5–100 ps is presented, which has not been feasible with previous ps-CARS measurements [16–19]. These are used to investigate the sensitivity of N\textsubscript{2}-RCARS temperature measurements to collisional energy transfer near 300-K, where J-level dependent dephasing is most prevalent.
2. Theory

The fs/ps RCARS technique developed in the current work is a variation of degenerate four-wave mixing (DFWM), which utilizes both fs and ps laser pulses to generate frequency-resolved rotational CARS spectra. As shown in Fig. 1(a), the pump, $\omega_1$, and Stokes, $\omega_2$, pulses are degenerate and spectrally broad. When the pulses are temporally overlapped as in Fig. 1(b), the difference-frequency between the pump and Stokes results in a broad excitation bandwidth. The impulsive excitation of the Raman coherence is particularly effective due to the multiple photon pairs which can mix to form a single difference frequency [24]. The induced coherent Raman polarization decays in time according to the molecular response function and is detected using a spectrally-narrowed degenerate probe pulse, $\omega_3$, which can be delayed in time, $\tau_{23}$, from the pump and Stokes pulses. The RCARS signal with frequency $\omega_{\text{CARS}} = \omega_1 - \omega_2 + \omega_3$ is a function of both resonant and nonresonant contributions and propagates with wavevector $k_{\text{CARS}} = k_1 - k_2 + k_3$ dictated by conservation of momentum.

**Fig. 1.** (a) Energy diagram for fs/ps RCARS illustrating spectral characteristics of pump ($\omega_1$), Stokes ($\omega_2$), probe ($\omega_3$), and CARS ($\omega_{\text{CARS}}$) beams, and (b) timing diagram of Gaussian probe-pulse generated by 4-f pulse shaper with time delay $\tau_{23}$ from pump and Stokes pulses.

A theoretical model for the pure-rotational hybrid fs/ps CARS spectra has been developed in accordance with the framework of Mukamel [30] based on previously published vibrational hybrid fs/ps CARS [28,31] and fs/ps RIKES models [32]. For a given probe delay, $\tau_{23}$, the rotational CARS signal, $I_{\text{CARS}}$, is proportional to the absolute square of the summation of the resonant, $P_{\text{Res}}$, and nonresonant, $P_{\text{NR}}$, induced third-order polarization as given in Eq. (1),

$$I_{\text{CARS}}(t, \tau_{23}) \propto \left| p_{\text{Res}}^{(3)}(t, \tau_{23}) + p_{\text{NR}}^{(3)}(t, \tau_{23}) \right|^2,$$

where the CARS intensity is a function of time, $t$, and probe delay. The frequency-domain spectrum is recovered via a Fourier transform of $I_{\text{CARS}}(t)$ while the time dependence comes through $\tau_{23}$. The nonresonant-induced third-order polarization is an important term during the temporal overlap of all three input beams, but may be neglected for delays $\tau_{23} \gg -\text{FWHM}$ of the probe pulse [28,29]. Neglecting the nonresonant term, the third-order polarization is given by Eq. (2),

$$P_{\text{Res}}^{(3)}(t, \tau_{23}) = \left( \frac{i}{\hbar} \right)^3 \int_0^\infty dt_1 \int_0^\infty dt_2 \int_0^\infty dt_3 \left[ R(t_1, t_2, t_3) E_i(t-t_1) \right. \left. \times E_r(t + \tau_{23} - t_3 - t_2) E_s(t + \tau_{23} - t_3 - t_2 - t_1) e^{i(\omega_1 - \omega_2 + \omega_3)t_1} e^{i(\omega_1 - \omega_2)t_2} e^{i\omega_1 t_1} \right].$$

where $R$ is the molecular response function, $E_i$, $E_r$, and $E_s$ are the electric field envelopes for the pump, Stokes, and probe pulses, respectively, with carrier frequencies $\omega$ and associated coherence time scales $t_1$, $t_2$, and $t_3$. Because the individual pump, Stokes, probe, and CARS pulses are far from any resonant transitions, it can be assumed that the molecular response (electronic dephasing) is rapid with respect to variations in the pump and Stokes pulses during the integration of $t_1$ and $t_2$ and the probe and CARS pulses during the integration of $t_3$ [28,31]. In this case we can replace $R(t_1, t_2, t_3)$ with $\delta(t_1)R(t_2)\delta(t_1)$ and simplify the expression for the third-order polarization to Eq. (3),
where the integrated term is the convolution of the pump and Stokes pulses with the molecular response function. A phenomenological model is used to describe the molecular response function of nitrogen where each transition from state $m$ to $n$ is given a frequency, $\omega_{mn}$, a collision-dominated Lorentzian linewidth, $\Gamma_{mn}$, and an intensity, $I_{mn}$, as in Eq. (4).

$$R(t) = \sum I_{nm}(T)e^{-i\omega_{mn}t}.$$

For pure rotational S-branch transitions ($\Delta v = 0$ and $\Delta J = \pm 2$), the frequency of each transition is defined as the difference between energy state $E_{v,J}$ and $E_{v,J+2}$. Each energy state is computed using fourth-order Herzberg molecular parameters accessible in the CARSFT molecular parameter files [33].

The intensity of each transition is calculated as a function of both the Raman transition cross-section, $(\partial \sigma / \partial \Omega)_J$, and the population difference, $\Delta \rho_{J,J+2}$, between the upper and lower energy states. The transition intensity and cross-section are given in Eq. (5) and Eq. (6),

$$I_{nm}(T) \propto \left( \frac{\partial \sigma}{\partial \Omega} \right)_J \Delta \rho_{J,J+2}(T),$$

$$\left( \frac{\partial \sigma}{\partial \Omega} \right)_J \propto \frac{4}{45} b_{J,J+2} (\gamma'^{2}) F(J),$$

where $b_{J,J+2}$ is the Placzek-Teller coefficient representing the overlap integral of the upper and lower energy state wavefunctions, $\gamma'$ is the polarization anisotropy, and $F(J)$ is a correction term for centrifugal distortion [34]. This correction for vibrational-rotational interaction is the so-called Herman-Wallis factor [35] and is defined in the current model using the formulation of Martinsson as shown in Eq. (7),

$$F(J) = 1 + 4.448 \left( \frac{2B_e}{\omega_e} \right)^2 (J^2 + 3J + 3),$$

where $B_e$ is the rotational constant, and $\omega_e$ is the vibrational frequency. Although this formulation has been recently questioned, the error associated with this assumption is minimal (<3 K) for the temperatures explored in the current work [35]. The population difference is a strong function of temperature, $T$, based on the Boltzmann distribution and also a function of the degeneracy of the lower energy state, $J$. For $N_2$, the rotational-nuclear degeneracy is dependent on $J$ level and mass number and results in an intensity contrast between odd and even numbered rotational levels [36].

The linewidth term is theoretically a function of Doppler and collisional broadening. For pressures greater than 1 atm, $N_2$ linewidths are dominated by collisional broadening and thus the individual Q-branch linewidths are computed using the Modified Exponential Gap (MEG) model with parameters from Rahn and Palmer [37]. The approximation for the S-branch rotational transition linewidth [38] is shown in Eq. (8).

$$\Gamma_{J,J+2} \approx \frac{1}{2} (\Gamma_{J,J} + \Gamma_{J+2,J+2}).$$

The linewidth (FWHM) is inversely related to a temperature-dependent term which modifies the linewidth for low rotational levels and is linearly related to pressure. The linewidth of each transition is especially important in temporally-resolved CARS techniques and it affects the decay in the CARS signal with increasing probe delay [16–19].
The optical Stark effect, which should be considered for ns CARS with high-intensity electric fields (~2 TW/cm$^2$·cm$^{-1}$) [39] is not included in the model. The total peak power used for single-shot measurements in the current work is ~0.5 TW/(cm$^2$·cm$^{-1}$). Also, for the nitrogen S-branch rotational transitions, Stark splitting can result in multiple lines with frequency shifts (~0.03 cm$^{-1}$) and beat frequencies (~1 ns) that are not detectable in the broadband, short-pulse arrangement of fs/ps RCARS.

3. Experimental setup

The 1.6-W output of a regeneratively amplified ultrafast laser (Solstice, Spectra-Physics) with a nominal pulse width of 100 fs and diameter of 5 mm is divided into two beams using a thin-film polarizer with a 15:1 ratio, as shown in Fig. 2. The high-power beam is reserved for the probe pulse, while the low-power beam is used to produce the 45-µJ pump and Stokes pulses with an additional ultrafast 50/50 beam-splitter. A 2.1 cm$^{-1}$ spectrally narrow probe pulse is generated using a folded 4/f pulse shaper with an adjustable square slit as previously reported by the authors [28,29]. The overall throughput of the pulse shaper at this spectral resolution is less than 1% resulting in a probe pulse energy of 10 µJ.

The temporal delay between the pump and Stokes pulses is minimized and held constant, while the delay of the probe pulse is set using a high-resolution motorized delay stage (ILS-150-PP, Newport). The parallel-polarized pump, Stokes, and probe beams are focused into the heated probe volume using a BOXcars phase-matching configuration [40] resulting in a cylindrical probe volume of 50-µm diameter and 1.1-mm length. To measure the diameter of the probe volume, a thin piece of aluminum is placed at the focal point and the hole produced by the beam is measured with a microscope. The interaction length is measured by passing a thin glass slide (190 µm) along the length of the probe volume and recording the 1/e$^2$ width of the resulting nonresonant signal. The CARS signal generated in N$_2$ is spatially filtered using an iris and focused into a 0.303-m spectrometer equipped with a 1200 line/mm grating (Shamrock SR-303i, Andor). The spectra are detected using an electron-multiplied charge-coupled device (EMCCD) camera capable of a 1-kHz non-EM acquisition rate and a 0.5-kHz rate in EM mode (DU-970P-UVB, Newton). The overall instrument resolution of the spectral detection system is measured to be 2.4 cm$^{-1}$ at 790 nm.

Nitrogen is heated using a 1500-W inline heating element and routed to a 0.75-inch diameter windowless cell. The flow rate for all conditions is 15 standard liters per minute to maximize heating and minimize flow disturbance. A K-type thermocouple (0.0625-inch-diameter) is inserted upstream of the cell and used to verify the nominal flow temperature after slight corrections for radiation heat transfer. Because the maximum heating temperature
is limited by cell design to 500 K, higher temperatures were measured in the exhaust of a stoichiometric $\text{H}_2$–$\text{air}$ flame with $\text{N}_2$ dilution to control the temperature.

4. Results and discussion

An important feature of hybrid fs/ps CARS is the generation of both fs and ps laser pulses using a single source. This setup is advantageous in that it ensures perfect synchronization between laser pulses and can be implemented in a straightforward manner. In the current work, a folded 4-$f$ pulse shaper is used to produce a narrowed probe linewidth of $\sim 2.1 \text{ cm}^{-1}$ (FWHM) from the broadband fs source, as shown in Fig. 3(a). This resolution is sufficient for spectrally resolving individual rotational transitions of the $\text{N}_2$ molecule, which exhibit an average separation of $\sim 8 \text{ cm}^{-1}$. The slightly asymmetric shape of the broadband source is accounted for in the theoretical modeling.

A cross-correlation of the probe pulse with the pump and Stokes pulses is recorded using nonresonant CARS signal in Argon. Unlike our previous work which used a sinc$^2$ lineshape, the current probe pulse exhibits a nearly transform-limited 8.4-ps Gaussian pulse shape in time, as shown in Fig. 3(b). A Gaussian pulse shape is advantageous over the sinc$^2$ profile since it does not exhibit the local minima and maxima associated with the sinc$^2$ pulse. Because of this, optimization of the probe-pulse delay for nonresonant suppression is simplified. To produce the nearly-Gaussian temporal pulse profile, the slit in the folded 4-$f$ pulse shaper is slightly rotated such that the edges of the slit were no longer perpendicular to the direction of dispersion. At small slit widths, this acts to smooth the edges of the otherwise square spectral profile of the probe beam. The nearly Gaussian spectral profile is evident in Fig. 3(a), which shows the convolution of the probe linewidth and instrument function.

Experimental spectrally-resolved $\text{N}_2$ spectra at time zero and a delay $\tau_{23} = 13.5$ ps are shown in Fig. 4 at 306 K. The spectrum at time zero is dominated by broad nonresonant background which must be modeled to accurately extract temperature and species concentration information. However, at a delay of 13.5 ps the nonresonant background has sufficiently decayed such that the spectrum is essentially nonresonant-background free. It is important to note that because the spacing between individual transitions is $\sim 8 \text{ cm}^{-1}$ for pure rotational S-branch transitions, the $2.1-\text{cm}^{-1}$ probe maintains sufficient spectral resolution to
resolve individual transitions, thus spectral fitting is straightforward. The slight increase in the baseline of the delayed spectrum is due to a small overlap of the instrument function with adjacent transitions.

Fig. 4. Experimental N\textsubscript{2} fs/ps RCARS spectra with 8.4-ps probe pulse delayed by 0 ps and 13.5 ps.

The time dynamics of the spectrally-integrated nonresonant signal from Argon and resonant signal from N\textsubscript{2} at 306 K and 500 K are given in Fig. 5. The open symbols represent experimental data points while the solid lines are simulations of the probe and resonant contributions as a function of time. Because the nonresonant contribution decays rapidly with respect to variations in the pump, Stokes and probe pulses, the nonresonant signal persists for only the duration of the probe pulse. The resonant signal in Fig. 5 is long lasting and displays a characteristic exponential decay. The rate of decay is highly dependent on internal energy transfer through molecular collisions [16], and detection within the first few ps reduces sensitivity to collisional energy transfer and greatly simplifies spectral interpretation [17–19]. The simulations of the time-dependent fs/ps RCARS signal at 306 K and 500 K are generated using the model described in the Theory section. The magnitude of the simulated data is adjusted to match the experimental intensities, although no adjustment was necessary for the time decay. Good agreement is found between the experimental and simulated time decays, with fs/ps RCARS exhibiting a relative signal-to-nonresonant-background ratio of ~800:1 at 13.5 ps for 306 K and 500 K.

Fig. 5. Normalized spectrally integrated fs/ps RCARS signal for nonresonant signal in Ar and spectrally-integrated resonant signal in pure N\textsubscript{2} at 306 K and 500 K. Open symbols represent experimental data and solid lines represent simulations.

The decay time constant of the rotational CARS spectra increases with an increase in temperature in accordance with a decrease in the linewidth [18,37]. This is in contrast to that observed for vibrational Q-branch CARS time-domain signals that decay more rapidly at higher temperature due to frequency-spread dephasing after the impulsive excitation [23]. Although the fs/ps RCARS signal normalized relative to time zero increases with temperature...
(see Fig. 5), the absolute signal decreases due to a drop in density and, therefore, N₂ concentration.

Although nonresonant suppression is not unique to fs/ps CARS [13–15,18], the advantage of fs/ps RCARS over pure fs CARS or pure ps CARS is the ability to achieve three orders of magnitude nonresonant suppression at sufficiently short probe delays for minimizing collisional effects, especially near 13.5 ps, while maintaining spectral resolution for frequency-domain detection. According to the data in Fig. 5, changes in the rate of collisional energy transfer from 306 K to 500 K are only significant beyond ~30 ps for the atmospheric-pressure conditions in this study.

It is well known that collisions between molecules can cause internal energy transfer which acts to decrease population of a given state as a function of time [37]. In the time domain, this manifests itself as a decrease in CARS signal strength as a function of time [41]. The decay rate is a strong function of thermodynamic properties, such as temperature, pressure, and molecular composition, that dictate the rate of collisions. The MEG model linearly relates the decay rate and pressure, while a more complex inverse relationship is given for the temperature and decay rate. In this way, for a given pressure the fastest rate of collisional energy transfer occurs at the lowest temperature, which is typically room temperature for many practical devices of interest. Additionally, the MEG model’s assumption of an exponential relationship between the rate of energy transfer and the energy difference between the initial and final states results in a decrease in the rate of energy transfer at higher rotational energy states [37]. This is due to the increased angular momentum of higher J levels, which take longer to decay. The FWHM of the spectral linewidth can be calculated from the time constant of the exponential decay using the formulation of Kulatilaka et al. [16] and is given as Eq. (9),

$$\Gamma_J = \frac{1}{2\pi c \tau_{CARS,J}}, \quad (9)$$

where \(\Gamma_J\) is the spectral linewidth in m⁻¹ of the transition with initial state \(J\), \(\tau_{CARS,J}\) is the time constant in seconds of a single-exponential function for the same transition, and \(c\) is the speed of light in m/s.

In traditional frequency-domain spectroscopy, the exponential decay of the CARS signal as a function of time is used to determine the spectral linewidth. The spectral shape takes the form of a Lorentzian function, the Fourier transform of the exponential decay. While fully frequency-domain techniques must model only the spectral linewidth effect of collisional energy transfer, time-domain spectroscopic techniques are directly sensitive to time-dependent signal decay. For both temporally- and spectrally-resolved techniques (ps RCARS or fs/ps RCARS) the collisional energy transfer is manifest in both domains. Experimentally measured spectra at 306 K and probe delays of 13.5 ps (typical of fs/ps RCARS) and 300 ps (typical of ps RCARS) are given in the inset of Fig. 6. Each spectrum is normalized to unity. Because the high J-level transitions experience a relatively slower decay at room temperature as compared to the low J levels, the spectrally-detected signal appears to shift to higher frequencies and therefore higher temperature. The intensity of each transition can be independently analyzed as a function of time and fit using a single exponential decay, as shown in Fig. 6(a).

The difference in decay rate is easily observed for the \(J = 6\) and \(J = 14\) transitions. Because of the temporal and spectral resolution, the decay rate of each transition can be measured and the experimental linewidth computed using Eq. (6). The resulting spectral linewidths are plotted as a function of J level for N₂-N₂ collisions at 306 K in Fig. 6(b). The measured linewidths agree well with the published Q-branch data from Rahn and Palmer [37] utilizing the approximation for S-branch transitions [38].
Fig. 6. Direct time-domain measurement of J-level dependent collisional linewidths at 306 K. (a) Experimental data for J = 6 and J = 14 transitions along with best-fit single-exponential decays. Inset illustrates perceived shift of fs/ps RCARS spectra to higher temperature from probe delay of 13.5 to 300 ps. (b) Measured linewidth for each transition and published linewidth from Ref. [37]. Error bars represent 95% confidence interval for exponential fit.

For ps RCARS, the perceived spectral shift can lead to a thermometry error of 46% at 360 ps, the time delay used in Ref 18, if the J-level dependent decay is not considered. The ability to neglect the effect of collisional energy transfer greatly simplifies the spectral simulation process and may reduce uncertainty in the measurement. For this reason, it is important to consider the accuracy of collision-free fs/ps RCARS temperature measurements as a function of probe delay. The best-fit temperatures for spectra at 306 K and 500 K are given in Fig. 7(a) as a function of probe delay both including (squares) and neglecting (circles) the time-dynamics of J-level dependent collisional linewidth. The corresponding error is plotted for both temperatures in Fig. 7(b). As expected, the full model which incorporates the collisional linewidth for each transition computes the temperature within 1% from 13.5 to 100 ps at both temperatures. If collisional energy transfer is neglected, the temperature bias at 306 K would reach 10% at 100 ps. For probe delays of ~150 ps or greater, typical of previous ps CARS measurements [18], the temperature bias is ~30% or greater and can lead to significant uncertainty if the gas temperature, density, or composition is varying in time. Because the effect of collisional energy transfer decreases with increased temperature, these effects may be ignored at high-temperature. However, for 300-500 K, it is anticipated that ps CARS measurements with ~100-ps pulses will require corrections of at least 10-30% due to collisional effects.

For probe delays less than 30 ps, however, there is no statistically significant difference between the collision-dependent and collision-free temperature measurements down to 300 K, which exhibit an error of ~1%. At atmospheric pressure, therefore, fs/ps RCARS thermometry can be performed while neglecting collisional energy transfer for temperatures greater than 300 K and probe delays less than 30 ps. This has implications for proper selection of the...
probe pulse delay. For nonresonant-free (~1000 × reduction) and collision-free (<1% error) measurements, the delay is limited to 13.5–30 ps in the current work. If systematic errors up to 2.5% and nonresonant contributions of 1% are acceptable, this interval could be extended to 10.5–50 ps. On the other hand, the range for collision-free measurements may be reduced at high pressure.

![Graph](image)

**Fig. 7.** (a) Best-fit temperature and (b) associated percent error as a function of probe delay for simulations with (solid squares) and without (open circles) time-dependent collisional energy transfer at 306 K and 500 K. Error bars represent a 1% uncertainty based on the data.

A significant advantage of fs/ps RCARS is the kHz repetition rate associated with ultrafast regenerative amplifiers, which is two to three orders of magnitude higher than current ns and ps sources used in CARS systems. To take advantage of the high repetition rates, accurate measurements must be possible using a single laser shot. An important factor when extracting temperature from an RCARS spectrum is the signal-to-noise ratio. The single-shot fs/ps RCARS spectra shown in Fig. 8 display an SNR of 3900:1 at 306 K, 425:1 at 500 K, and 42:1 at 700 K. The residual is shown shifted by −0.1. A probe-pulse delay of 13.5 ps is used in all three cases, ensuring that the temperature bias due to collisions or nonresonant background is negligible. Hence, these spectra have sufficient SNR for best-fit temperatures to be extracted from the theoretical model with high accuracy. Single-shot spectra at 800 K were also collected while keeping all laser parameters constant, leading to an SNR of ~15:1 and representing the upper limit of single-shot temperature measurements for the current laser configuration. Application of this approach to higher temperatures by increasing the probe-pulse bandwidth (i.e., throughput of the 4-f pulse shaper) or by employing a laser with increased laser energy is the subject of future investigation.
Fig. 8. Single-shot pure-rotational hybrid fs/ps RCARS spectra of N$_2$ at (a) 306 K, (b) 500 K, and (c) 700 K. Open symbols represent experimental data while solid lines represent best fit simulations. Residual is shown shifted by $-0.1$.

5. Conclusions

Single-shot, collision- and nonresonant-background-free, pure-rotational hybrid fs/ps CARS thermometry of N$_2$ is demonstrated using a kHz-rate fs laser source. By delaying the 8.4-ps probe pulse by 13.5 ps after the arrival of the 100-fs pump and Stokes pulses, it is possible to achieve a signal-to-nonresonant-background ratio of 800:1. The current approach also allows direct measurements of $J$-level dependent dephasing rates in the range of 13.5 to 100 ps, which are used to show that measured temperatures are collision free (to within 1% or less) for probe delays below 30 ps at atmospheric pressure. Using a frequency- and time-domain model, best-fit temperatures for current RCARS spectra at a probe delay of 13.5 ps exhibit accuracies of $\sim$1% in the range of 306 K to 700 K without the need for corrections due to nonresonant background or collisions. This model is also used to show that the temperature bias due to collisions (i.e., $J$-level dependent dephasing) can be corrected for probe delays beyond 30 ps. The temperature correction at 100 ps, for example, is $\sim$10% near 300 K. This
has important implications for the effects of collisions when using ps CARS with ~100-ps
pulses; this approach can require probe delays of at least 150 ps to avoid nonresonant
background, leading to temperature corrections of ~30% or more. Hence, the collision- and
nonresonant-background-free fs/ps-RCARS approach can reduce uncertainty in unsteady
flows where temperature, density, or composition may fluctuate in time. This is achieved
using a kHz-rate fs laser source, although new amplified laser sources can potentially allow
measurements up to 10 kHz or beyond. Future work includes extension to higher
temperatures using increased pulse energies and studies of collisional effects at higher
pressure.

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