Interference-free gas-phase thermometry at elevated pressure using hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering

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Abstract: Rotational-level-dependent dephasing rates and nonresonant background can lead to significant uncertainties in coherent anti-Stokes Raman scattering (CARS) thermometry under high-pressure, low-temperature conditions if the gas composition is unknown. Hybrid femtosecond/picosecond rotational CARS is employed to minimize or eliminate the influence of collisions and nonresonant background for accurate, frequency-domain thermometry at elevated pressure. The ability to ignore these interferences and achieve thermometric errors of <5% is demonstrated for N2 and O2 at pressures up to 15 atm. Beyond 15 atm, the effects of collisions cannot be ignored but can be minimized using a short probe delay (~6.5 ps) after Raman excitation, thereby improving thermometric accuracy with a time- and frequency-resolved theoretical model.

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1. Introduction

Coherent anti-Stokes Raman scattering (CARS) is a highly accurate and precise nonlinear spectroscopic technique that has been utilized for the measurement of gas-phase temperature in a wide range of reacting and non-reacting flows [1]. While CARS offers excellent chemical specificity and efficient signal collection, measurement errors from composition-dependent interferences, such as collisional energy transfer and nonresonant background, significantly complicate the analysis, particularly in high-pressure environments [2]. As shown in previous work, interferences from nonresonant background can be suppressed in the frequency domain using polarization techniques [3] or by temporally separating the probe pulse from the pump and Stokes pulses [4–6]. Temporal suppression has been demonstrated for both vibrational [7] and rotational CARS [8], but the temporal probe delays in previous work were sufficiently long (~100 ps) that the rovibrational and rotational spectra were sensitive to the effects of collisions on individual rotational transitions, especially at low temperature. In fact, much of the early work in time-domain fs and ps CARS utilized this sensitivity to measure molecular and collision-dependent parameters [9]. This included the effects of collisions on Q-branch line-shift parameters [10], rotational constants [11], and rotational energy transfer models [12–14] for several molecules of interest in combustion (H2, N2, CO, and C2H2). Such
measurements were intended to provide critical information for modeling the composition-dependent line widths of gas-phase spectra for accurate thermometry.

When the gas composition is not known a priori, however, it is advantageous to avoid entirely the effects of collisions. Whereas previous ultrafast CARS temperature measurements exploited features of the molecular response at long delay times and, therefore, required detailed modeling of collisional effects [15], more recent efforts have instead utilized the initial (<15 ps) decay rate of the Raman excitation, which occurs through non-collisional, frequency-spread dephasing [16]. Frequency-spread dephasing of the vibrational manifold is much faster than collisional dephasing for pressures up to 10 atm [16]; therefore, uncertainties due to the complex collisional environment can be avoided. However, single-shot detection in the time domain requires chirped-probe detection [1, 15], and interference-free measurements beyond 1 atm have yet to be demonstrated using this approach. Hence it is not possible at this time to ascertain the accuracy of interference-free, chirped-probe fs CARS at elevated pressures.

As an alternative to time-domain detection, it is of interest to determine if measurements that are free of collisions and nonresonant-background can be achieved using frequency-domain thermometry at high pressure. Recently, the authors demonstrated a hybrid fs/ps CARS technique that employed 100-fs pump and Stokes pulses to induce coherent vibrational or pure rotational Raman oscillations in N\textsubscript{2} while probing the molecular response using a frequency-narrowed, time-delayed 1–10 ps probe pulse [17–20]. In this approach, a short (0.3–10 ps) probe-pulse delay was sufficient to avoid overlap with the pump and Stokes pulses to eliminate nonresonant background, while the transform-limited ps pulse allowed for single-shot frequency-domain detection of individual N\textsubscript{2} rotational [17] or vibrational transitions [18]. In the current work, we investigate the ability of hybrid fs/ps rotational coherent anti-Stokes Raman scattering (RCARS) to avoid the effects of collisions and nonresonant background for accurate, interference-free thermometry at high pressure. The ability to avoid collisional effects at high pressure is of particular interest for frequency-domain thermometry, which typically carries inherent sensitivity to rotational-level-dependent linewidths in the case of ns or ps CARS. The ability of the current approach to isolate individual rotational transitions enables detailed analysis of the effects of rotational-level-dependent dephasing rates on thermometric accuracy. Expanding the technique to include fs/ps RCARS thermometry of O\textsubscript{2}, we use a phenomenological model to compare the relative effects of collisions on N\textsubscript{2} and O\textsubscript{2} spectra for probe delays of 6.5 to 150 ps at elevated pressure. For conditions in which collisions cannot be avoided (beyond 15 atm), we evaluate the feasibility of improving temperature accuracy by minimizing the effects of collisions with short probe delays and including the collisional linewidth in a time- and frequency-resolved theoretical model.

2. Theory and experiment

A detailed theoretical treatment of hybrid fs/ps CARS and experimental description can be found elsewhere [17, 21]. For pure S-branch transitions (Δν = 0, ΔJ = + 2), the molecular response from the pump (ω\textsubscript{pump}) and Stokes (ω\textsubscript{Stokes}) pulses is treated phenomenologically as a function of time, t, in Eq. (1),

\[ R(t) = \sum I_{J+2,J} e^{-i\omega_{J+2,J} t - \Gamma_{J+2,J} t} \]

where each transition is assigned an intensity, \( I_{J+2,J} \), a frequency (s\(^{-1}\)), \( \omega_{J+2,J} \), and linewidth (s\(^{-1}\)), \( \Gamma_{J+2,J} \) [17, 21]. The transition intensity \( I_{J+2,J} \) is not a function of time, but is highly dependent on temperature, \( T \). The response decays exponentially with a time constant \( T_{J+2,J} = \Gamma_{J+2,J}^{-1} \). The linewidth is highly temperature and pressure dependent, displaying a linear dependence on pressure and more complex inverse relationship with temperature [22]. Because low rotational states decay more rapidly than high rotational states, the spectral and
temporal features of the CARS signal begin to mimic higher temperatures at long delay times [8, 17, 23]. The resulting thermometric error is more pronounced at low temperature where the difference between linewidths of low and high rotational states is largest [8, 17]. At higher pressure, rapid collisional dephasing can also significantly enhance rotational energy transfer and require detection at short delay times for accurate interference-free thermometry.

\( \text{N}_2 \) and \( \text{O}_2 \) CARS spectra were recorded at 298 and 295 K, respectively, from 1 to 20 atm. The pure gases were pressurized in a cylindrical stainless-steel vessel, and the temperature was measured with a 1/16-inch diameter K-type thermocouple and pressure with a digital pressure gauge (0–500 ± 1.25 psi). The frequency-dispersed CARS signal is detected using a 0.303-m spectrometer (1200 line/mm) with sufficient resolution for distinguishing individual rotational transitions. The signal can be numerically integrated over the entire S-branch (~10–200 cm\(^{-1}\)) as given in Fig. 1 for \( \text{N}_2 \) and \( \text{O}_2 \) at pressures of 1, 2.5, 5, 10, 15, and 20 atm, or numerically integrated over a single transition.

\[ \text{Fig. 1. Spectrally integrated hybrid fs/ps RCARS signals from 1 to 20 atm for N}_2\text{–N}_2\text{ collisions at 298 K, and O}_2\text{–O}_2\text{ collisions at 295 K. The solid lines are theoretical simulations and the data are normalized to the nonresonant background.} \]

The solid lines in Fig. 1 represent simulations using a time- and frequency-domain theoretical model with modified exponential gap (MEG) linewidth parameters from Seeger et al. [2] and S-branch linewidths approximated following Martinsson et al. [24]. The individual linewidths vary as a function of initial rotational state, \( J \), decreasing as \( J \) is increased. Thus the low rotational states exhibit higher rates of energy transfer and decay at a faster rate than high rotational states. As highlighted in our previous publications [17,20], the linewidth varies from 0.098 cm\(^{-1}\) to 0.063 cm\(^{-1}\) from \( J = 4 \) to 18 for \( \text{N}_2 \), and 0.107 cm\(^{-1}\) to 0.064 cm\(^{-1}\) for \( N = 5 \) to 23 for \( \text{O}_2 \). Since each transition decays at a different rate, the CARS spectra appear to shift to higher temperatures as the low rotational states decay rapidly with increased probe delay. The experimentally measured time decays are well predicted by the theoretical model in Fig. 1 and illustrate the short time window between nonresonant background and strong collisional dephasing at high pressure. The dephasing rate for \( \text{N}_2 \) is faster than that of \( \text{O}_2 \), which implies that \( \text{N}_2 \) CARS thermometry will be more sensitive to collisions.
3. Results and discussion

Because of rapid collisional dephasing at high pressure, the probe-pulse spectral bandwidth was increased from previous work (2.1 cm\(^{-1}\)) \[17\] to 3.6 cm\(^{-1}\) (4.1 ps) to achieve a minimum probe delay of 6.5 ps (~1000 \times nonresonant suppression). This bandwidth is sufficient to avoid spectral overlap of the transitions so that the effects of rotational energy transfer can be clearly observed in the frequency-domain spectra. For illustration, experimental O\(_2\) spectra are presented in Fig. 2 at fixed delays of (a) 6.5 and (b) 25 ps and pressures of 1 atm and 10 atm (symbols). The theoretical O\(_2\) spectrum (solid lines) assumes a pressure of 1 atm. At a probe delay of 6.5 ps, shown in Fig. 2(a), the difference between the two experimental spectra is negligible, leading to best-fit temperatures that are within 4% of 295 K. This illustrates the independence from collisional effects at short probe delays. For the longer probe delay of 25 ps, as shown in Fig. 2(b), the experimental spectrum at 1 atm is nearly the same as that shown at 6.5 ps. However, for a probe delay of 25 ps and a pressure of 10 atm, the spectrum shows an apparent population shift towards higher rotational states, leading to a best-fit temperature of 342 K. This represents an error of 16%.

![Fig. 2. Spectrally resolved hybrid fs/ps RCARS spectra of O\(_2\) at 1 atm and 10 atm and probe delays of (a) 6.5 ps and (b) 25 ps. The best fit temperatures neglecting collisional energy transfer are given and the solid line represents the best fit spectra at 1 atm.](image)

As noted earlier avoiding the effects of collisions is important when the gas composition is not known \textit{a priori}, but at elevated pressure this requires that the probe pulse be shorter than and arrive sooner than 25 ps. To evaluate the potential for interference-free measurements from 1 to 20 atm, the thermometric error was investigated from a minimum probe delay of 6.5 ps (to avoid nonresonant background) to a maximum of 150 ps (typical of ps CARS with probe pulses of ~80 ps or higher). This investigation was performed by fitting the time-dependent spectra using a spectral database where the linewidth was set to zero in the molecular response function (Eq. (1)) for all rotational transitions. Best-fit temperatures are
plotted as a function of probe delay in Figs. 3(a) and 4(a). The constant solid line represents 
the actual temperature, and the constant dashed lines represent ± 5% error.

The data of Figs. 3(a) and 4(a) show the quantitative impact of collisions on thermometric 
error associated with N\textsubscript{2} or O\textsubscript{2} CARS spectra at elevated pressure. At the shortest probe delay 
of 6.5 ps, for example, the thermometric error without corrections for nonresonant 
background or collisional energy transfer is <5% up to 15 atm. This error is slightly higher 
than that previously reported using validated RCARS models for high resolution frequency 
domain thermometry at elevated pressure [2, 25]. However, it should be noted that the 
measurements presented here differ substantially from previous frequency-domain 
experiments since the composition-dependent Raman linewidth component of the molecular 
response function is neglected. Hence, sensitivity to linewidth variations due to changes in gas 
composition would also be reduced or eliminated. This is an important finding because 
corrections for linewidth variations increase model complexity and are difficult to 
approximate in gas mixtures with unknown composition. Moreover, the error associated with
collisional effects is further reduced at higher temperature [8, 17] such that interference-free measurements may be possible beyond 15 atm in heated flows.

Near room temperature, the interference-free assumption is limited even for probe delays as short as 6.5 ps where the error increases to 9% at 20 atm, thus requiring corrections for the effects of collisions. In cases for which corrections are necessary, however, the current data indicate that the use of short probe delays significantly reduces the impact of collisions and minimizes the corresponding corrections for rotational-level-dependent dephasing with the time- and frequency-resolved theoretical model. As shown in Figs. 3(b) and 4(b), the theoretical simulation with linewidths from the MEG model predicts temperatures that are within 5% of the known temperatures for all pressures and probe delays. At shorter probe delays (<100 ps), the accuracy is improved to 2.5% for all pressures, and at the shortest probe delay (6.5 ps), the accuracy improves to 1% for all pressures. The fact that the theoretical fit is improved at shorter probe delays is indicative of reduced interference from collisional effects, which could be critical in environments with unknown species compositions. Since the composition is known in this case, the increase in thermometric error at 150 ps may be partially attributed to uncertainties in linewidths derived from the MEG model, as well as uncertainties due to the Q-branch approximation. By minimizing the necessary corrections, the fs/ps hybrid RCARS approach reduces the effects of errors associated with uncertainties in linewidth.

To characterize further the sensitivity to collisional dephasing and predict thermometric errors for arbitrary pressures and probe delays, we utilized a phenomenological model, Eq. (2), that captures the increase in thermometric error with pressure and time (as indicated by the solid lines in Figs. 3 and 4),

\[
T_{\text{App}}(\tau_{23}, P) = (1 - a_1 P)T_o \exp\left(\left(a_2 P^2 + a_3 P\right) \tau_{23}\right)
\]

where \(T_{\text{App}}\) is the apparent temperature with the collision-free assumption (K), \(\tau_{23}\) is the probe delay (ps), \(T_o\) is the reference temperature (K), \(P\) is the pressure (atm), and \(a_i\) are fit parameters. The coefficients have been determined with a fair degree of consistency from 1 to 20 atm and at room temperature for N\(_2\) (\(a_1 = 7.36 \times 10^{-3} \text{ atm}^{-1}\), \(a_2 = 4.257 \times 10^{-5} \text{ atm}^{-2} \text{ps}^{-1}\), and \(a_3 = 1.016 \times 10^{-3} \text{ atm}^{-1} \text{ps}^{-1}\)) and for O\(_2\) (\(a_1 = 1.405 \times 10^{-3} \text{ atm}^{-1}\), \(a_2 = 1.563 \times 10^{-5} \text{ atm}^{-2} \text{ps}^{-1}\), and \(a_3 = 4.77 \times 10^{-4} \text{ atm}^{-1} \text{ps}^{-1}\)). The reduced sensitivity of O\(_2\) to collisional effects at elevated pressure is quantified by the lower values of \(a_2\) and \(a_3\) in the exponential term in Eq. (2). This is due to greater uniformity in linewidth across the rotational energy levels of O\(_2\). This simple model can also be used to estimate the probe delay, \(\tau_{23}\), and the associated minimum probe pulse width necessary for avoiding the effects of collisions at even higher pressures with frequency-domain ps or fs/ps CARS thermometry. At 20 atm, for example, the temperature shift is as high as 14.5 K/ps for N\(_2\) and 5.7 K/ps for O\(_2\). Without this knowledge, the use of longer probe delays or slight jitter between the preparation and probe pulses can cause significant variations in the apparent temperature (as high as 5% per ps).

4. Conclusions

In summary, we have quantified the effects of pressure on hybrid fs/ps CARS thermometric errors for both N\(_2\) and O\(_2\) up to 20 atm. Utilizing fs pump and Stokes pulses and a probe-pulse delay of 6.5 ps, it is possible to avoid the effects of collisions for pressures up to 15 atm and minimize corrections for collisional effects at even higher pressures. This can be achieved while avoiding nonresonant background and isolating individual rotational transitions for accurate frequency-domain thermometry. Future work will focus on testing the interference-free assumption at higher temperatures and pressures.
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