2012

Communication: Hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering thermometry using a narrowband time-asymmetric probe pulse

Han U. Stauffer  
*Spectral Energies*

Joseph D. Miller  
*Iowa State University*

Sukesh Roy  
*Spectral Energies*

James R. Gord  
*Air Force Research Laboratory*

Follow this and additional works at: [http://lib.dr.iastate.edu/me_pubs](http://lib.dr.iastate.edu/me_pubs)  
🔗 Part of the [Mechanical Engineering Commons](http://lib.dr.iastate.edu/me_pubs/159)

The complete bibliographic information for this item can be found at [http://lib.dr.iastate.edu/me_pubs/159](http://lib.dr.iastate.edu/me_pubs/159). For information on how to cite this item, please visit [http://lib.dr.iastate.edu/howtocite.html](http://lib.dr.iastate.edu/howtocite.html).
Communication: Hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering thermometry using a narrowband time-asymmetric probe pulse

Abstract
A narrowband, time-asymmetric probe pulse is introduced into the hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering (fs/ps RCARS) technique to provide accurate and precise single-shot, high-repetition-rate gas-phase thermometric measurements. This narrowband pulse-generated by inserting a Fabry-Pérot étalon into the probe-pulse beam path-enables frequency-domain detection of pure-rotational transitions. The unique time-asymmetric nature of this pulse, in turn, allows for detection of resonant Raman-active rotational transitions free of signal contamination by nonresonant four-wave-mixing processes while still allowing detection at short probe-pulse delays, where collisional dephasing processes are negligible. We demonstrate that this approach provides excellent single-shot thermometric accuracy (1 error) and precision (~2.5) in gas-phase environments.

Keywords
cohherent anti-Stokes Raman scattering, dephasing process, femtoseconds, four-wave-mixing process, frequency domains, fasphase, high repetition rate, narrow bands, nonresonant, probe pulse, rotational transition, signal contamination, probes

Disciplines
Mechanical Engineering

Comments
The following article appeared in Journal of Chemical Physics 136, 111101 (2012); and may be found at doi: 10.1063/1.3693669.

Rights
Copyright 2012 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.
Communication: Hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering thermometry using a narrowband time-asymmetric probe pulse


Citation: The Journal of Chemical Physics 136, 111101 (2012); doi: 10.1063/1.3693669

View online: http://dx.doi.org/10.1063/1.3693669

View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/136/11?ver=pdfcov

Published by the AIP Publishing

Articles you may be interested in

Time- and frequency-dependent model of time-resolved coherent anti-Stokes Raman scattering (CARS) with a picosecond-duration probe pulse

Analysis of time resolved femtosecond and femtosecond/picosecond coherent anti-Stokes Raman spectroscopy: Application to toluene and Rhodamine 6G

Communication: Time-domain measurement of high-pressure N2 and O2 self-broadened linewidths using hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering

Direct measurement of rotationally resolved H2 Q-branch Raman coherence lifetimes using time-resolved picosecond coherent anti-Stokes Raman scattering
Appl. Phys. Lett. 97, 081112 (2010); 10.1063/1.3483871

Femtosecond coherent anti-Stokes Raman scattering measurement of gas temperatures from frequency-spread dephasing of the Raman coherence
Communication: Hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering thermometry using a narrowband time-asymmetric probe pulse


Spectral Energies, LLC, 5100 Springfield St., Suite 301, Dayton, Ohio 45431, USA
Department of Mechanical Engineering, Iowa State University, Ames, Iowa 50011, USA
Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson AFB, Ohio 45433, USA

(Received 13 January 2012; accepted 15 February 2012; published online 16 March 2012)

A narrowband, time-asymmetric probe pulse is introduced into the hybrid femtosecond/picosecond rotational coherent anti-Stokes Raman scattering (fs/ps RCARS) technique to provide accurate and precise single-shot, high-repetition-rate gas-phase thermometric measurements. This narrowband pulse—generated by inserting a Fabry-Pérot étalon into the probe-pulse beam path—enables frequency-domain detection of pure-rotational transitions. The unique time-asymmetric nature of this pulse, in turn, allows for detection of resonant Raman-active rotational transitions free of signal contamination by nonresonant four-wave-mixing processes while still allowing detection at short probe-pulse delays, where collisional dephasing processes are negligible. We demonstrate that this approach provides excellent single-shot thermometric accuracy (<1% error) and precision (~2.5%) in gas-phase environments. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3693669]

Time-resolved optical probe techniques have long been utilized as robust non-invasive diagnostics of gas-phase environments, and four-wave mixing techniques, such as coherent anti-Stokes Raman scattering (CARS), have played a crucial role in the development of increasingly sensitive and accurate temperature measurements.1,2 As pulsed-laser technology has advanced toward higher repetition rates and shorter pulse durations—from nanoseconds (ns) to picoseconds (ps) to femtoseconds (fs)—over the past few decades, a variety of CARS techniques have been developed to take advantage of these improvements and provide accurate and precise single-shot thermometric measurements at repetition rates of 1 kHz and greater.3 One approach that seeks to exploit simultaneously the time- and frequency-domain properties of sub-ns pulses is hybrid fs/ps CARS.4-6 This technique, which combines two temporally overlapped broadband, fs-duration initial pulses (pump and Stokes) with a time-delayed narrowband, ps-duration final pulse (probe),4 exhibits several advantages over other purely ps- or fs-time-resolved CARS approaches. In particular, the impulsive pump/Stokes pulses provide coherent excitation of multiple rotational5,8 or rovibrational5,7 transitions. The inclusion of a narrowband, ps-duration probe provides an ideal compromise of temporal and spectral resolution; the former allows detection that is outside the time window in which nonresonant (NR) components contaminate the CARS signal yet short compared to collisional decay timescales,8 whereas the latter is necessary to observe spectrally resolved rotational or rovibrational features.

Here, we describe a unique implementation of hybrid fs/ps rotational CARS (RCARS) in which the ps-duration probe pulse is generated by placing an air-spaced Fabry-Pérot étalon in the beam path of a broadband fs-duration pulse. This produces a probe with a Lorentzian frequency-domain line shape narrow enough to resolve rotational transitions of gas-phase species such as nitrogen (N2). Such spectral resolution, which is substantially higher than previous vibrational fs/ps CARS measurements using a Lorentzian bandwidth filter,7 is critical for single-shot RCARS thermometry.6 This approach also represents an extremely straightforward application of the CARS optical probe technique, requiring only a single amplified ultrafast laser system with traditional optical components and delay lines. No parametric upconversion, as is required for vibrational CARS probes using nondegenerate pulses, and no 4-f pulse shaping configurations, used to generate the ps-duration probe pulse in most previous implementations of fs/ps CARS,4,5,9 are required. As was recognized first in surface sum-frequency generation experiments by Lagutchev et al.,10 another beneficial aspect of such a pulse is that it exhibits an asymmetric time-domain profile with a rapid (sub-ps) onset followed by a longer exponential decay—a direct result of the Fourier-transform relationship between the time-domain pulse and the corresponding frequency-domain Lorentzian line shape. Whereas a similar notch-filter-shaped asymmetric probe pulse has been used in single-beam CARS measurements of liquid-phase species,11 the three-pulse configuration used here allows continuous adjustment of the asymmetric-probe-pulse delay. Thus, we demonstrate the benefits associated with this time-asymmetric probe pulse through example measurements of N2 gas, including the ability to measure frequency-resolved rotational spectra at very short time delays (≤2 ps), allowing detec-

a)Author to whom correspondence should be addressed. Electronic mail: hans.stauffer.ctr@wpafb.af.mil.
tion prior to significant collisional dephasing while avoiding NR background. This is notably shorter than \((1/7 \times 1/3)\) the delays used in previous fs/ps CARS measurements, which relied on probe-pulse amplitude-shaping schemes to create symmetric time-domain pulses with \([\text{sinc}(t)]^2\) intensity profiles.\(^6,8,9\) Also in contrast with previous fs/ps RCARS measurements,\(^6,8\) a time-asymmetric probe pulse allows the temporal resolution of individual pure-rotational recurrences, enabling frequency-domain detection of interference effects associated with the evolving rotational wave packet.

The optical system and temperature-controlled cell used here have been described previously.\(^6\) These experiments differ in the use of a time-asymmetric ps probe pulse, which is generated by insertion of a Fabry-Pérot étalon [TecOptics, free spectral range (FSR) = 250 cm\(^{-1}\), finesse = 45] into the probe-beam pathway to produce a spectrum with a Lorentzian linewidth of \(\sim 5.6\) cm\(^{-1}\) centered at 800 nm. This linewidth allows resolution of \(N_2\) rotational \(S\)-branch transitions yet decays on a time scale (1/e decay time: 0.9 ps) that is rapid compared to collisional dephasing lifetimes. Numerical simulations of the observed signals were carried out using a time-dependent CARS model that allows explicit inclusion of molecular and pulse electric-field parameters as well as interfering NR CARS signal that is observed when the probe pulse overlaps the pump/Stokes pair.\(^6,8\) The time-asymmetric probe pulse used in these simulations is modeled as a Lorentzian line shape matching the experimental probe spectrum.

A schematic depicting the time evolution associated with this experimental approach is presented in Fig. 1. The three RCARS input pulses include two degenerate broadband fs-duration pulses, which provide excitation of several accessible rotational Raman \(\Delta J = +2\) (\(S\)-branch) transitions. These pulses induce the resonant molecular response, \(R(t)\), depicted in Fig. 1(a) for room-temperature \(N_2\), that exhibits a highly periodic time-domain structure typical of RCARS transitions.\(^12–14\) The repeating peaks correspond to fractional time scales associated with a full classical rotational period of \(\tau_{\text{full}} = n(2\hbar c)^{-1}\), where \(n\) is an integer, \(c\) is the speed of light, and \(B_0\) is the rigid-rotor rotational constant \(B_0 = 1.99\) cm\(^{-1}\) for \(N_2\); \(\tau_{\text{full}} = 8.38\) ps); integer multiples of quarter-rotational and half-rotational recurrences are also observed.\(^14\) The simulated time-asymmetric probe pulse is shown in Fig. 1(b). The use of this pulse allows detection of NR-free signal at much shorter time delays, when collisional dephasing is negligible. In this case, the calculated first full recurrence at \( \approx 8.4 \text{ ps} \) exhibits a \(\sim 15\%\) intensity decay relative to the purely resonant response at \( t = 0 \) under 1-bar conditions [Fig. 1(a)], so measurements at partial recurrences (at 2.10 ps and 4.15 ps, \(\pi/2\) time scales associated with a full classical rotational period of \(\tau_{\text{full}}\)) are necessary to reduce or remove collisional effects.

The fractional and full recurrences can be understood from a simple physical standpoint,\(^12\) since they describe the rephasing motions of an ensemble of rotors with \(J\)-dependent angular frequencies \(\omega_J = (1/2)J(J+1)\omega_0\), where \(\omega_0 = 4\pi B_0 c\) is the fundamental rotational frequency.\(^12,14\) The evolution of the initially prepared rotational wave packets is depicted in Figs. 1(c)–1(h) for several selected times following initiation of the \(N_2\) rotational response by linearly polarized impulsive pump and Stokes pulses. These together prepare an evolving superposition of states with angular alignment described by \(Y_{M+2}^J(\theta, \phi) \cdot \cos^2 \theta \cdot Y_{M}^J(\theta, \phi)d\phi\), where \(J\) is the lower rotational state for a given \(S\)-branch transition [denoted \(S(J)\)], and \(Y_{M}^J(\theta, \phi)\) are spherical harmonics describing the \(|J, M\rangle\) rotational sublevel.\(^14\) Because even-\(J\) and odd-\(J\) transitions exhibit self-similar alignment behavior, evolving angular distributions for superpositions of even-\(J\) and odd-\(J\) states are depicted separately in Fig. 1 for illustrative purposes; the full molecular response results from a coherent sum of these two contributions. Time evolution of these coherences results from an oscillating term for each transition, \(\exp[i(\omega_{J+2} - \omega_J)t]\), resulting in a time-dependent accumulated phase. Thus, the relative phase accumulation for a given \(S(J)\) transition during one full recurrence is \((4J + 6)\pi \eta = 0\) (modulo \(2\pi\)), and all states within the superposition interfere constructively. At fractional \((\eta = 1/4, 1/2, 3/4, \text{ etc.})\) recurrences, each transition has an accumulated relative phase of \((4J + 6)\pi \eta\), so the relative phases of all transitions at the half-recurrence are equal to \((2J + 3)\pi = \pi\) (modulo \(2\pi\)) for both even and odd \(J\) [Fig. 1(f)]. At the quarter recurrence...
are equally populated; however, the nuclear-spin statistics
\( \frac{-\pi}{2} \) result from the even transition; the alternating peak intensity pattern observed
nearly no temporal dependence. One reference peak is
spans multiple recurrences, the simulated signal exhibits
rotational lines; however, since this simulated probe pulse
in a frequency-domain spectrum that exhibits well-separated
contributions to the observed signal, as evidenced both by
the absence of obvious NR contribution to the earlier 2.10-ps
probe-delay signal and by the fact that the simulated spectra
included in Fig. 2(b), each containing no NR contribution, exhibit excellent agreement at both of these delays.

To explore further the probe-pulse-delay dependence
observed in the CARS signal, additional fine-step time-
dependence measurements were made over the 0–5 ps time
scale (Fig. 3). Figures 3(a) and 3(b) show, respectively, experi-
mental and simulated contour plots of the time-dependent
CARS signal measured using this time-asymmetric probe
pulse. Excellent agreement is observed, with the exception of
the odd-J S-branch lines in the 2.10-ps results. Additionally, although both even- and odd-J peaks are present in the 4.15-ps spectrum, a broad background is also observed. This background results from the fact that the probe-pulse
bandwidth (5.6 cm\(^{-1}\)) is comparable to the rotational line spacing, \( 4B_0 \sim 8 \text{ cm}^{-1} \), giving rise to constructive interference between the Lorentzian-line-shape wings of each individual peak. Most notably, this background does not result from NR
contributions to the observed signal, as evidenced both by
the absence of obvious NR contribution to the earlier 2.10-ps
probe-delay signal and by the fact that the simulated spectra
included in Fig. 2(b), each containing no NR contribution, exhibit excellent agreement at both of these delays.

To explore further the probe-pulse-delay dependence
observed in the CARS signal, additional fine-step time-
dependence measurements were made over the 0–5 ps time
scale (Fig. 3). Figures 3(a) and 3(b) show, respectively, experi-
mental and simulated contour plots of the time-dependent
CARS signal measured using this time-asymmetric probe
pulse. Excellent agreement is observed, with the exception of
the odd-J S-branch lines in the 2.10-ps results. Additionally, although both even- and odd-J peaks are present in the 4.15-ps spectrum, a broad background is also observed. This background results from the fact that the probe-pulse
bandwidth (5.6 cm\(^{-1}\)) is comparable to the rotational line spacing, \( 4B_0 \sim 8 \text{ cm}^{-1} \), giving rise to constructive interference between the Lorentzian-line-shape wings of each individual peak. Most notably, this background does not result from NR
contributions to the observed signal, as evidenced both by
the absence of obvious NR contribution to the earlier 2.10-ps
probe-delay signal and by the fact that the simulated spectra
included in Fig. 2(b), each containing no NR contribution, exhibit excellent agreement at both of these delays.

To explore further the probe-pulse-delay dependence
observed in the CARS signal, additional fine-step time-
dependence measurements were made over the 0–5 ps time
scale (Fig. 3). Figures 3(a) and 3(b) show, respectively, experi-
mental and simulated contour plots of the time-dependent
CARS signal measured using this time-asymmetric probe
pulse. Excellent agreement is observed, with the exception of
the odd-J S-branch lines in the 2.10-ps results. Additionally, although both even- and odd-J peaks are present in the 4.15-ps spectrum, a broad background is also observed. This background results from the fact that the probe-pulse
bandwidth (5.6 cm\(^{-1}\)) is comparable to the rotational line spacing, \( 4B_0 \sim 8 \text{ cm}^{-1} \), giving rise to constructive interference between the Lorentzian-line-shape wings of each individual peak. Most notably, this background does not result from NR
contributions to the observed signal, as evidenced both by
the absence of obvious NR contribution to the earlier 2.10-ps
probe-delay signal and by the fact that the simulated spectra
included in Fig. 2(b), each containing no NR contribution, exhibit excellent agreement at both of these delays.

To explore further the probe-pulse-delay dependence
observed in the CARS signal, additional fine-step time-
dependence measurements were made over the 0–5 ps time
scale (Fig. 3). Figures 3(a) and 3(b) show, respectively, experi-
mental and simulated contour plots of the time-dependent
CARS signal measured using this time-asymmetric probe
pulse. Excellent agreement is observed, with the exception of
the odd-J S-branch lines in the 2.10-ps results. Additionally, although both even- and odd-J peaks are present in the 4.15-ps spectrum, a broad background is also observed. This background results from the fact that the probe-pulse
bandwidth (5.6 cm\(^{-1}\)) is comparable to the rotational line spacing, \( 4B_0 \sim 8 \text{ cm}^{-1} \), giving rise to constructive interference between the Lorentzian-line-shape wings of each individual peak. Most notably, this background does not result from NR
contributions to the observed signal, as evidenced both by
the absence of obvious NR contribution to the earlier 2.10-ps
probe-delay signal and by the fact that the simulated spectra
included in Fig. 2(b), each containing no NR contribution, exhibit excellent agreement at both of these delays.

To explore further the probe-pulse-delay dependence
observed in the CARS signal, additional fine-step time-
dependence measurements were made over the 0–5 ps time
scale (Fig. 3). Figures 3(a) and 3(b) show, respectively, experi-
mental and simulated contour plots of the time-dependent
CARS signal measured using this time-asymmetric probe
pulse. Excellent agreement is observed, with the exception of
the odd-J S-branch lines in the 2.10-ps results. Additionally, although both even- and odd-J peaks are present in the 4.15-ps spectrum, a broad background is also observed. This background results from the fact that the probe-pulse
bandwidth (5.6 cm\(^{-1}\)) is comparable to the rotational line spacing, \( 4B_0 \sim 8 \text{ cm}^{-1} \), giving rise to constructive interference between the Lorentzian-line-shape wings of each individual peak. Most notably, this background does not result from NR
contributions to the observed signal, as evidenced both by
the absence of obvious NR contribution to the earlier 2.10-ps
probe-delay signal and by the fact that the simulated spectra
included in Fig. 2(b), each containing no NR contribution, exhibit excellent agreement at both of these delays.
adjacent peak. At the quarter recurrence, in contrast, even-
J S-branch lines have accumulated relative phases of \(-\pi/2\) (modulo 2\(\pi\)), whereas odd-J lines have accumulated relative
phases of \(\pi/2\) (modulo 2\(\pi\)); each S-branch line is exactly out-of-
phase with each adjacent peak. The frequency-domain res-
olution dictated by the chosen linewidth of the probe pulse re-
sults in the partial overlap of these adjacent lines, resulting in
essentially a complete destructive interference of the weaker
odd-J transitions at the quarter-rotational recurrence.

Because the intended application of this time-asymmetric
probe approach to fs/ps RCARS is for high-repetition-rate
thermometry in low-temperature combustion environments,
it is important to note the accuracy and precision associated
with single-shot measurements at these two delays, partic-
ularly given the fact that the observed spectra at these two
delays are notably different. One thousand single-shot spec-
tra were recorded in a heated-cell environment \((T = 540 \text{ K})\)
at both the quarter- and half-rotational recurrence delays.
Following optimization of several laser-dependent parame-
ters using room-temperature \(\text{N}_2\) spectra, least-squares fits to
temperature-dependent simulated spectra were carried out for
each single-shot spectrum in the time series. The resultant
probability distribution functions and example fit single-shot
spectra for each time delay are reported in Fig. 4. Excellent
accuracy is observed, with corresponding precision (one-\(\sigma\) )
of \(\sim 2.5\%\), independent of the choice of partial recurrence; the
absence of odd-J rotational lines at the shorter-delay (2.10-ps)
recurrence does not reduce the temperature precision. This
is particularly important under turbulent conditions that are
typically encountered in real-world high-pressure combus-
tion environments, where collisional dephasing time scales be-
come comparable to these probe delay times and local species
number densities are unknown or fluctuating, necessitating
short-delay measurements. Experiments are currently under-
way to explore directly the ability of this time-asymmetric
probe fs/ps CARS approach to detect important combustion
species in high-pressure environments, both in single-species
conditions and in mixtures.

Funding was provided, in part, by the National Science
Foundation (NSF) (CBET-1056006, Dr. Arvind Atreya, Pro-
gram Official), the Air Force Office of Scientific Research
(Dr. Enrique Parra, Program Manager), and the Air Force Re-
search Laboratory (AFRL) under Contract No. FA8650-10-C-
2008. J.D.M. was supported by the National Science Foundation
Graduate Fellowship Program.