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

Joseph D. Miller
Iowa State University

Sukesh Roy
Spectral Energies

James R. Gord
Air Force Research Laboratory

Terrence R. Meyer
Iowa State University, trm@iastate.edu

Follow this and additional works at: http://lib.dr.iastate.edu/me_pubs

Part of the Mechanical Engineering Commons

The complete bibliographic information for this item can be found at http://lib.dr.iastate.edu/me_pubs/166. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.
Communication: Time-domain measurement of high-pressure N2 and O2 self-broadened linewidths using hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering

Abstract
The direct measurement of self-broadened linewidths using the time decay of pure-rotational hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering (fs/ps RCARS) signals is demonstrated in gas-phase N2 and O2 from 1–20 atm. Using fs pump and Stokes pulses and a spectrally narrowed ps probe pulse, collisional dephasing rates with time constants as short as 2.5 ps are captured with high accuracy for individual rotational transitions. S-branch linewidths of N2 and O2 from ∼0.06 to 2.2 cm−1 and the line separation of O2 triplet states are obtained from the measured dephasing rates and compared with high-resolution, frequency-domain measurements and S-branch approximations using the modified exponential gap model. The accuracy of the current measurements suggests that the fs/ps RCARS approach is well suited for tracking the collisional dynamics of gas-phase mixtures over a wide range of pressures.

Keywords
cohherent anti-Stokes Raman scattering, current measurements, dephasing rates, direct measurement, frequency domain measurement, gasphase, modified exponential gaps, probe pulse, rotational transition, optical pumping, Raman spectroscopy

Disciplines
Mechanical Engineering

Comments

Rights
Copyright 2011 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: Time-domain measurement of high-pressure N2 and O2 self-broadened linewidths using hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering

Citation: The Journal of Chemical Physics 135, 201104 (2011); doi: 10.1063/1.3665932
View online: http://dx.doi.org/10.1063/1.3665932
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/135/20?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Direct measurement of S-branch N2-H2 Raman linewidths using time-resolved pure rotational coherent anti-Stokes Raman spectroscopy

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

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

Femtosecond time resolved coherent anti-Stokes Raman spectroscopy of H 2 – N 2 mixtures in the Dicke regime: Experiments and modeling of velocity effects

Elucidating the spectral and temporal contributions from the resonant and nonresonant response to femtosecond coherent anti-Stokes Raman scattering
Communication: Time-domain measurement of high-pressure N\textsubscript{2} and O\textsubscript{2} self-broadened linewidths using hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering


1Department of Mechanical Engineering, Iowa State University, Ames, Iowa 50011, USA
2Spectral Energies, LLC, Dayton, Ohio 45431, USA
3Air Force Research Laboratory, Propulsion Directorate, Wright-Patterson Air Force Base, Ohio 45433, USA
4Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-University Erlangen-Nürnberg, Erlangen, Germany

(Received 6 October 2011; accepted 15 November 2011; published online 28 November 2011)

The direct measurement of self-broadened linewidths using the time decay of pure-rotational hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering (fs/ps RCARS) signals is demonstrated in gas-phase N\textsubscript{2} and O\textsubscript{2} from 1–20 atm. Using fs pump and Stokes pulses and a spectrally narrowed ps probe pulse, collisional dephasing rates with time constants as short as 2.5 ps are captured with high accuracy for individual rotational transitions. S-branch linewidths of N\textsubscript{2} and O\textsubscript{2} from \(\sim 0.06\) to \(2.2\) cm\(^{-1}\) and the line separation of O\textsubscript{2} triplet states are obtained from the measured dephasing rates and compared with high-resolution, frequency-domain measurements and S-branch approximations using the modified exponential gap model. The accuracy of the current measurements suggests that the fs/ps RCARS approach is well suited for tracking the collisional dynamics of gas-phase mixtures over a wide range of pressures. © 2011 American Institute of Physics.

[doi:10.1063/1.3665932]

The use of femtosecond (fs) and picosecond (ps) laser sources for gas-phase coherent anti-Stokes Raman scattering (CARS) thermometry has grown significantly in recent years due to the high peak powers of these laser sources and interest in resolving the time dynamics of the molecular response.\(^1\) In fs CARS, the temporally short and spectrally broad (transform-limited) pump and Stokes pulses allow highly efficient, in-phase, and impulsive excitation of the entire rovibrational or pure-rotational manifold.\(^1\) In this case, the molecular response is resolved in time using the spectrally integrated signal, but the dephasing rate of individual (J-level) transitions cannot be measured directly.\(^2\) In ps CARS, the ability to measure short time decays is limited by relatively long pump, Stokes, and probe pulse widths (typically \(\sim 100\) ps) and by the need to avoid nonresonant background by temporally separating the probe pulse from the pump and Stokes pulses.\(^4\) For measurements of collisional dephasing rates, especially at high pressure, the ideal approach is to utilize broad (fs) pump and Stokes pulses and a spectrally narrowed (ps) probe pulse that can simultaneously isolate each molecular transition while still resolving short \(\sim\)ps decay times.

Recently, the authors demonstrated a hybrid fs/ps CARS technique that uses 100-fs pump and Stokes pulses to impulsively excite vibrational or pure rotational transitions of a molecule and a spectrally narrowed, 1–10 ps probe pulse for frequency-domain thermometry.\(^2\) A similar single-beam approach using a pulse-shaped 7-fs pulse to produce the pump, Stokes, and probe pulses via phase and polarization discrimination has been demonstrated, although the spectral resolution was limited to \(\sim 5\) cm\(^{-1}\) by the spatial light modulator.\(^9\) The hybrid fs/ps CARS approach offers the ability to temporally discriminate against nonresonant background, similar to either fs or ps CARS, but has the unique capability to resolve gas-phase rotational spectra within several hundred fs after Raman excitation.\(^10\) These features are ideal for studying the time dynamics of individual rotational transitions at elevated pressure. Above 1 atm, the linewidths of N\textsubscript{2} and O\textsubscript{2} can be considered purely pressure broadened, and Doppler contributions to the linewidth can be neglected. Hence, detection of collisional decay rates for rotational transitions using fs/ps CARS allows for direct measurement of spectral linewidths.\(^7\)

In this work, a time- and frequency-resolved fs/ps rotational CARS (RCARS) technique is used to accurately measure and report self-broadened S-branch linewidths of N\textsubscript{2} and O\textsubscript{2} from 1–20 atm. Few direct measurements of self-broadened S-branch linewidths are reported in the literature, and many ps and ns rotational CARS models rely on S-branch approximations from Q-branch data which can lead to errors at high pressure.\(^11\) These measurements are critical for the determination of temperature and relative species concentrations in gas-phase media, especially at high pressure, because rotational-level and species-dependent collisional dephasing rates can alter the Raman spectra and lead to significant measurement errors.\(^4\)

The hybrid fs/ps RCARS system has been described previously\(^7\) and is summarized briefly in this communication. The pump and Stokes pulses were derived from the 100-fs output of a regeneratively amplified Ti:sapphire laser centered at \(\sim 790\) nm. The energy of each pulse was 40 \(\mu\)J
at atmospheric pressure and was decreased at elevated pressure to avoid stimulated Raman pumping and interference from sustained molecular alignment. A 2-cm$^{-1}$ full width at half maximum (FWHM), 8.1-ps probe pulse was formed in a 4-f pulse shaper by spectrally filtering the beam using a square slit. This bandwidth was sufficient to isolate individual transitions while minimizing the probe delay for nonresonant suppression. The slit was slightly rotated to produce a nearly Gaussian time-domain profile.$^7$ The three beams were focused in a BOXCARS phase-matching configuration using a 300-mm lens. The CARS beam was spatially filtered and then detected using a 0.303-m spectrometer with a 1200 line/mm grating and an electron-multiplied charge-coupled device camera. The gases were pressurized in a cylindrical stainless steel vessel equipped with a 1/16-inch diameter K-type thermocouple and digital pressure gauge (0–500 ±1.25 psi).

A theoretical description of the hybrid fs/ps RCARS process is given in Refs. 7, 8, and 13. Of particular interest here is the treatment of the molecular response function. For pure rotational transitions ($\Delta v = 0$), a phenomenological function is given as the summation of all active O-branch ({$\Delta J = -2$}) and S-branch transitions ({$\Delta J = +2$}) from state $m$ to $n$

$$ R(t) = \sum I_{n,m}(T) e^{-i\omega_{n,m}t} \Gamma_{n,m}, $$

where $I_{n,m}$ is the intensity of each rotational Raman transition as a function of temperature$^7$ and $\omega_{n,m}$ (s$^{-1}$) is the frequency of each transition. The linewidth, $\Gamma_{n,m}$ (s$^{-1}$), is related to the S-branch spectral linewidth (m$^{-1}$, FWHM) and decay constant, $\tau_{\text{CARS},J+2,J}$ (s)

$$ \Gamma_{J+2,J|\omega} = 2\pi c \Gamma_{J+2,J|\omega} = (\tau_{\text{CARS},J+2,J})^{-1}, $$

where $c$ is the speed of light (m/s)$^5$ The linewidth represents a single-exponential decay of the molecular response in time primarily due to inelastic molecular collisions.$^2,14$ The modified exponential gap (MEG) model is frequently employed to calculate the transition dependence (initial state $m$) of the collisional linewidth assuming a linear dependence on pressure.$^14$ In this work, comparisons are made with the MEG model using parameters for self-broadened $N_2$ and $O_2$ from Seeger $et$ $al.$$^{11}$ and the rotational approximation of Martinsson $et$ $al.$$^{15}$

For simple linear molecules such as $N_2$, the rotational levels are well known and the rotational transitions are indicated by the total angular momentum, $J$, of the initial state. For $O_2$, the ground state exhibits a nuclear spin of zero and an electronic spin, $S$, of one which leads to a splitting of the rotational states into triplets.$^{16,17}$ In this case, the rotational transitions are given as a function of the rotational quantum number, $N$, of the initial state while the splitting occurs due to the $N$–$S$ coupling with the total angular momentum given by $J = (N - 1, N, N + 1)$.$^{16}$

Rotationally resolved RCARS signals of $N_2$ (298 K) and $O_2$ (295 K) are shown as a function of probe delay in Fig. 1 for pressures of 1, 10, and 20 atm. Three independent scans for each pressure were performed over a one week period to verify the repeatability. Only the $J = 4$ and 14 transitions for $N_2$ and $N = 5$ and 15 transitions for $O_2$ are shown for simplicity. The RCARS signals are compared to the normalized and spectrally integrated nonresonant background from argon to show the relative rates of decay. The time constant of each rotational transition was measured by fitting a single exponential function to the decay of the RCARS signal spectrally integrated over each individual transition, and the spectral linewidth was computed using Eq. (2). For most conditions, the fitting process was initiated after a probe delay of 10.5 ps when the nonresonant background dropped by 10$^2$, as shown in Fig. 1. At a fixed probe delay, however, the relative influence of the nonresonant background increased at higher

FIG. 1. Spectrally resolved hybrid fs/ps RCARS signals from $J = 4$ and 14 for $N_2$ at (a) 1 atm, (b) 10 atm, and (c) 20 atm and $N = 5$ and 15 for $O_2$ at (d) 1 atm, (e) 10 atm, and (f) 20 atm. Solid lines are exponential fits to signal decay.
pressure because the resonant signal was sensitive to collisions. To offset this effect, the fitting process for rotational transitions with the lowest signal levels was initiated at longer delays (≥ 12 ps) to allow the nonresonant background to decay even further. This ensured that the signal-to-nonresonant ratio in the spectral band of each transition, estimated from the nonresonant susceptibilities of Ar, N₂, and O₂, was always 10² or higher.

The measured self-broadened S-branch linewidths are shown in Fig. 2 at pressures of 1, 10, and 20 atm and tabulated for pressures of 1, 2.5, 5, 10, 15, and 20 atm in Tables I and II. The uncertainty was calculated from the 95% confidence interval of the average fit with an additional systematic experimental uncertainty (~2%) combined in quadrature. The 95% confidence interval of the average data is comparable to the standard deviation from the three individual datasets. Generally, the S-branch linewidths were measured with 1%–2% uncertainty at 1 atm, which represents an improvement over previous frequency-domain measurements under similar conditions. At the highest pressure of 20 atm, the decay rate constant is as small as 2.5 ps, leading to higher uncertainties for low and high rotational transitions of N₂ and O₂ and odd transitions of N₂.

The solid lines in Fig. 2 represent self-broadened linewidths for N₂ and O₂ computed using the MEG model Q-branch linewidths derived from frequency-domain measurements with the S-branch approximation. The computed linewidths agree well with the current data for N₂ but deviate at low rotational levels as found in previous time-domain and frequency-domain measurements at 1 atm. This shift is due to re-orientation of the molecular axis after collisions, which does not contribute to Q-branch linewidths from which the MEG model was derived.

The O₂ measured linewidths for high rotational numbers are in agreement with the MEG model at 1 atm and with previous S-branch measurements using spontaneous Raman

![Figure 2](image-url)

**FIG. 2.** Measured (a) N₂ and (b) O₂ self-broadened linewidths as a function of initial rotational state at pressures of 1, 10, and 20 atm. Solid lines are MEG linewidths using S-branch approximation. Bars represent calculated uncertainty.

### TABLE I. Experimental N₂ self-broadened linewidths, FWHM (cm⁻¹).

<table>
<thead>
<tr>
<th>J</th>
<th>1 atm</th>
<th>2.5 atm</th>
<th>5 atm</th>
<th>10 atm</th>
<th>15 atm</th>
<th>20 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.266 ± 0.020</td>
<td>0.505 ± 0.023</td>
<td>0.954 ± 0.060</td>
<td>1.518 ± 0.186</td>
<td>2.140 ± 0.099</td>
<td>2.158 ± 0.162</td>
</tr>
<tr>
<td>4</td>
<td>0.259 ± 0.016</td>
<td>0.490 ± 0.025</td>
<td>0.946 ± 0.074</td>
<td>1.505 ± 0.233</td>
<td>1.993 ± 0.141</td>
<td>1.993 ± 0.141</td>
</tr>
<tr>
<td>5</td>
<td>0.262 ± 0.017</td>
<td>0.468 ± 0.017</td>
<td>0.943 ± 0.040</td>
<td>1.397 ± 0.174</td>
<td>1.891 ± 0.129</td>
<td>1.891 ± 0.129</td>
</tr>
<tr>
<td>6</td>
<td>0.256 ± 0.017</td>
<td>0.456 ± 0.019</td>
<td>0.917 ± 0.043</td>
<td>1.357 ± 0.162</td>
<td>1.956 ± 0.134</td>
<td>1.956 ± 0.134</td>
</tr>
<tr>
<td>7</td>
<td>0.236 ± 0.015</td>
<td>0.441 ± 0.015</td>
<td>0.895 ± 0.034</td>
<td>1.335 ± 0.157</td>
<td>1.772 ± 0.230</td>
<td>1.772 ± 0.230</td>
</tr>
<tr>
<td>8</td>
<td>0.233 ± 0.015</td>
<td>0.428 ± 0.015</td>
<td>0.882 ± 0.037</td>
<td>1.278 ± 0.170</td>
<td>1.850 ± 0.129</td>
<td>1.850 ± 0.129</td>
</tr>
<tr>
<td>9</td>
<td>0.226 ± 0.015</td>
<td>0.430 ± 0.015</td>
<td>0.858 ± 0.029</td>
<td>1.252 ± 0.152</td>
<td>1.649 ± 0.222</td>
<td>1.649 ± 0.222</td>
</tr>
<tr>
<td>10</td>
<td>0.221 ± 0.014</td>
<td>0.398 ± 0.015</td>
<td>0.814 ± 0.033</td>
<td>1.192 ± 0.175</td>
<td>1.678 ± 0.130</td>
<td>1.678 ± 0.130</td>
</tr>
<tr>
<td>11</td>
<td>0.203 ± 0.013</td>
<td>0.383 ± 0.014</td>
<td>0.798 ± 0.027</td>
<td>1.162 ± 0.149</td>
<td>1.553 ± 0.214</td>
<td>1.553 ± 0.214</td>
</tr>
<tr>
<td>12</td>
<td>0.199 ± 0.013</td>
<td>0.362 ± 0.020</td>
<td>0.783 ± 0.030</td>
<td>1.088 ± 0.178</td>
<td>1.594 ± 0.090</td>
<td>1.594 ± 0.090</td>
</tr>
<tr>
<td>13</td>
<td>0.194 ± 0.013</td>
<td>0.358 ± 0.014</td>
<td>0.717 ± 0.026</td>
<td>1.051 ± 0.150</td>
<td>1.466 ± 0.235</td>
<td>1.466 ± 0.235</td>
</tr>
<tr>
<td>14</td>
<td>0.191 ± 0.015</td>
<td>0.314 ± 0.018</td>
<td>0.747 ± 0.051</td>
<td>0.926 ± 0.172</td>
<td>1.597 ± 0.105</td>
<td>1.597 ± 0.105</td>
</tr>
<tr>
<td>15</td>
<td>0.173 ± 0.012</td>
<td>0.308 ± 0.016</td>
<td>0.643 ± 0.028</td>
<td>0.931 ± 0.145</td>
<td>1.435 ± 0.239</td>
<td>1.435 ± 0.239</td>
</tr>
<tr>
<td>16</td>
<td>0.265 ± 0.050</td>
<td>0.637 ± 0.092</td>
<td>0.790 ± 0.186</td>
<td>1.522 ± 0.294</td>
<td>1.522 ± 0.294</td>
<td>1.522 ± 0.294</td>
</tr>
<tr>
<td>17</td>
<td>0.246 ± 0.025</td>
<td>0.548 ± 0.055</td>
<td>0.815 ± 0.147</td>
<td>1.316 ± 0.272</td>
<td>1.316 ± 0.272</td>
<td>1.316 ± 0.272</td>
</tr>
</tbody>
</table>

This table shows experimental N₂ self-broadened linewidths for different rotational quantum numbers (J) at various pressures (1 atm, 2.5 atm, 5 atm, 10 atm, 15 atm, 20 atm). The linewidths are given in FWHM (cm⁻¹) with uncertainties. The data is consistent with the MEG model predictions.
scattering. The linewidths of the low rotational states are influenced by the triplet ground state of the O₂ molecule, which exhibits three transitions (S₁, S₀, and S₋₁) separated by ~1.99 cm⁻¹. Because the triplet is spectrally overlapped by the probe pulse, this separation results in a temporal oscillation of the RCARS signal, as shown in Fig. 3 for N = 1 and 3 at 1 atm. A cosine function is used to fit the oscillation with resulting periods of 16.8 ps and 16.9 ps for N = 1 and 3, respectively. These represent separations of 1.98 cm⁻¹ and 1.97 cm⁻¹, which are within 1% of theoretical and experimental values. While the intensity of the triplets are of the same order for N = 1, they are negligible for N > 5. At elevated pressure, the CARS signal decays significantly within the first period of the triplet oscillation; thus, the oscillation cannot be resolved, and the measured linewidths may be larger than expected due to interference of the triplet oscillation. For this reason we have not reported linewidth data for N = 1 and 3 in this work.

In summary, hybrid fs/ps RCARS was used to measure the collisional decay rates and individual S-branch transition linewidths of N₂ and O₂ from 1–20 atm. Excellent sensitivity to transition-resolved signal decay was achieved at high pressures where the rate constants are as low as 2.5 ps. Agreement was found with previous N₂ and O₂ S-branch measurements at low pressure which indicate a small positive offset from the MEG model. This relationship was confirmed at high pressures. The accuracy for low J levels of N₂ at higher pressure was bounded by a combination of nonresonant background, small decay rate constants, and low spectral intensity. In the case of O₂, oscillations in the time decay due to interference of the triplet ground state limited the accuracy of linewidth measurements for low rotational states.

Funding was provided by the National Science Foundation (CBET-1056006, Dr. A. Atreya, Program Official) and the Air Force Office of Scientific Research (Dr. R. Parra and Dr. C. Li, Program Managers). J. Miller was supported by the National Science Foundation Graduate Fellowship Program. The authors also thank C. Dedic, M. Johnson, and B. Halls of Iowa State University.


**TABLE II.** Experimental O₂ self-broadened linewidths, FWHM (cm⁻¹).

<table>
<thead>
<tr>
<th>N</th>
<th>1 atm</th>
<th>2.5 atm</th>
<th>5 atm</th>
<th>10 atm</th>
<th>15 atm</th>
<th>20 atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.107 ± 0.002</td>
<td>0.244 ± 0.015</td>
<td>0.459 ± 0.017</td>
<td>1.006 ± 0.051</td>
<td>1.329 ± 0.039</td>
<td>1.881 ± 0.145</td>
</tr>
<tr>
<td>7</td>
<td>0.093 ± 0.001</td>
<td>0.221 ± 0.013</td>
<td>0.434 ± 0.016</td>
<td>0.866 ± 0.040</td>
<td>1.282 ± 0.036</td>
<td>1.646 ± 0.070</td>
</tr>
<tr>
<td>9</td>
<td>0.088 ± 0.001</td>
<td>0.212 ± 0.013</td>
<td>0.420 ± 0.014</td>
<td>0.840 ± 0.036</td>
<td>1.243 ± 0.034</td>
<td>1.588 ± 0.056</td>
</tr>
<tr>
<td>11</td>
<td>0.086 ± 0.001</td>
<td>0.213 ± 0.013</td>
<td>0.409 ± 0.015</td>
<td>0.815 ± 0.039</td>
<td>1.200 ± 0.039</td>
<td>1.569 ± 0.067</td>
</tr>
<tr>
<td>13</td>
<td>0.084 ± 0.001</td>
<td>0.209 ± 0.013</td>
<td>0.398 ± 0.015</td>
<td>0.787 ± 0.036</td>
<td>1.155 ± 0.039</td>
<td>1.523 ± 0.050</td>
</tr>
<tr>
<td>15</td>
<td>0.080 ± 0.001</td>
<td>0.196 ± 0.012</td>
<td>0.374 ± 0.015</td>
<td>0.749 ± 0.035</td>
<td>1.114 ± 0.039</td>
<td>1.485 ± 0.061</td>
</tr>
<tr>
<td>17</td>
<td>0.075 ± 0.001</td>
<td>0.186 ± 0.012</td>
<td>0.353 ± 0.015</td>
<td>0.714 ± 0.032</td>
<td>1.034 ± 0.042</td>
<td>1.448 ± 0.051</td>
</tr>
<tr>
<td>19</td>
<td>0.072 ± 0.001</td>
<td>0.183 ± 0.012</td>
<td>0.333 ± 0.017</td>
<td>0.676 ± 0.025</td>
<td>0.968 ± 0.040</td>
<td>1.406 ± 0.062</td>
</tr>
<tr>
<td>21</td>
<td>0.069 ± 0.001</td>
<td>0.168 ± 0.012</td>
<td>0.310 ± 0.023</td>
<td>0.635 ± 0.027</td>
<td>0.927 ± 0.068</td>
<td>1.380 ± 0.056</td>
</tr>
<tr>
<td>23</td>
<td>0.064 ± 0.002</td>
<td>0.163 ± 0.016</td>
<td>0.261 ± 0.055</td>
<td>0.552 ± 0.054</td>
<td>0.807 ± 0.144</td>
<td>1.329 ± 0.134</td>
</tr>
</tbody>
</table>

**FIG. 3.** Decay of N = 1 and 3 rotational lines of O₂. Solid lines show measured oscillations due to triplet ground state with periods of 16.8 ps and 16.9 ps, respectively.