Ultrafast-laser-induced backward stimulated Raman scattering for tracing atmospheric gases

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Abstract: By combining tunable broadband pulse generation with the technique of nonlinear spectral compression we demonstrate a prototype scheme for highly selective detection of air molecules by backward stimulated Raman scattering. The experimental results allow to extrapolate the laser parameters required for standoff sensing based on the recently demonstrated backward atmospheric lasing.

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1. Introduction

Many applications in environmental science and homeland security call for standoff identification of airborne pollutants with the highest possible sensitivity and chemical specificity. Optical techniques such as Light Detection and Ranging (LIDAR) and differential LIDAR (DIAL) offer powerful tools for the remote sensing of trace gases and aerosols (including hazardous species) in the atmosphere [1, 2], proving useful for environment protection, meteorology, geosciences, archeology, forestry, agriculture, and homeland security. LIDAR systems based on Raman scattering allow a fingerprinting of molecules using their unique vibrational spectral signatures, providing a high degree of chemical specificity [3]. Rapidly progressing coherent LIDAR technologies [2] push the frontiers of advanced atmospheric research, enabling high-sensitivity and high-resolution atmospheric wind profiling. The success of heterodyne detection as a cornerstone concept of the existing coherent LIDAR approaches inspires a broader use of coherent processes and methods, motivating the development of optical remote sensing strategies where the use of coherence is not limited to the detection of the backscattered signal return, but is used to provide a highly directional backward optical signal through coherent Raman scattering [4–7], thus enhancing the sensitivity and selectivity of standoff detection. However, with fully ground-based laser systems, delivering only forward beams, generation of coherent backward signals is prohibited by momentum conservation, manifested as the phase-matching condition in coherent wave mixing. The search for the solutions to this fundamental problem is ongoing, with the latest theoretical proposals including the use of electromagnetically induced coherent backscattering [8], plasma-assisted backscattering [9], as well as combinations of laser and radar methods [10]. The recent discovery of remotely pumped lasing in the atmosphere, using atomic oxygen [11] or molecular nitrogen [12], provides a unique remote source of coherent backward radiation. It is due to this discovery that the long-standing challenge of backward coherent optical signal generation, needed to enhance sensitivity and selectivity of coherent remote sensing, can now be experimentally confronted. Here, we report the first proof-of-the-principle experiments demonstrating ultrafast backward coherent Raman scattering as a promising technique for the chemically specific remote sensing of trace gases in the atmosphere.

Coherent Raman scattering techniques require simultaneous excitation of the molecular specimen with two beams, the pump (at frequency $\omega_p$) and the Stokes (at frequency $\omega_S$) with frequency detuning matching a molecular vibration, $\omega_p - \omega_S = \Omega$. Coherent antiStokes Raman scattering (CARS) detects the signal at the antiStokes frequency, $\omega_{\text{AS}} = 2\omega_p - \omega_S$. Stimulated Raman scattering (SRS) is a pump-probe technique, detecting the stimulated Raman gain (SRG) of the Stokes or the stimulated Raman loss (SRL) of the pump. For the purpose of...
remote sensing, SRS offers the following important advantages with respect to CARS: (i) it is inherently phase-matched, thus allowing the implementation of a backward interaction geometry, which would be impossible using CARS due to wavevector mismatch [7]; (ii) it is free from the non-resonant background originated by the electronic contributions to the third-order nonlinear susceptibility [13, 14]; (iii) its signal scales linearly with the number of probed molecular oscillators, thus allowing the detection of relatively low-concentration specimens. The main experimental challenge of SRS resides in the difficulty to measure the weak SRG/SRL sitting on top of an intense (possibly noisy) Stokes/pump pulse.

![Conceptual scheme of remote atmospheric sensing using backward SRS from an atmospheric laser. For details see text. The desired tunability range of the pump (Stokes) radiation is determined by taking into account the Raman shift of H₂ molecule at atmospheric pressure, which amounts to 4155 cm⁻¹.](image)

The conceptual scheme of a standoff backward SRS experiment is shown in Fig. 1: it requires the combination of the backward propagating, remotely pumped atmospheric N₂ or O₂ laser (acting as a Stokes(pump) beam) with a synchronized, narrowband tunable laser beam sent in the forward direction (acting as a pump(Stokes) beam). When the frequency difference between the pump and Stokes matches the Raman resonance of the molecule to be detected, then the backward propagating beam experiences SRG (SRL), enabling sensitive molecular fingerprinting. For spectral resolution, both pump and Stokes need to be narrowband and at least one needs to be broadly tunable in order to address different resonances. Since the atmospheric probe laser is already narrowband and at a fixed frequency, we plan to generate a tunable narrowband pump by nonlinear frequency conversion of the laser pulses generated by the same laser system that initiates the atmospheric lasing.

As an intermediate goal toward employing an atmospheric 337-nm N₂ laser in the future, in this work we experimentally and theoretically investigate a prototype for backward SRS in air. The experimental approach is based on a laser system from which we derive narrowband UV pulses, imitating the N₂ laser emission from a filament and acting as Stokes pulses, and synchronized tunable narrowband UV pump pulses. As model systems we study responses from atmospheric nitrogen and oxygen as well as methane in a variable pressure cell. Based on the results of the studies we are in a position to extrapolate the laser parameters required for a real remote sensing experiment.

2. Requirements for a backward SRS experiment

It is worth reminding that for an SRS process, in the weak signal and monochromatic plane wave limits, one can write: $\Delta I_p \propto -\text{Im}(\chi^{(3)}) I_p I_s L$, $\Delta I_s \propto +\text{Im}(\chi^{(3)}) I_p I_s L$, where $I_p$ and $I_s$
are the pump and Stokes intensities respectively, \( L \) is the interaction length and \( \chi^{(3)} \) is the nonlinear Raman susceptibility of the transition under study. One can thus measure either the SRG of the Stokes beam:

\[
SRG = \frac{\Delta I_s}{I_s} \propto \text{Im} \left( \chi^{(3)} \right) I_p L
\]  

(1)

or the SRL of the pump beam:

\[
SRL = \frac{\Delta I_p}{I_p} \propto -\text{Im} \left( \chi^{(3)} \right) I_s L
\]  

(2)

As it is illustrated in Fig. 1, it is apparent that the pump and Stokes beams are fully interchangeable. It is thus convenient to use the more intense beam to induce a large stimulated signal and measure the intensity variations of the weaker “probe” beam, detected either as SRG or as SRL.

For a given value of \( \chi^{(3)} \) (which depends on substance to be detected and concentration), the two parameters that determine the strength of the SRS signal are the peak intensity of the pump (Stokes) pulse \( I_s(I_p) \) and the interaction length \( L \). For a given available pulse energy, the peak intensity scales inversely with pulse duration, so that shorter pulses give higher SRS signals; on the other hand, the pulse bandwidth should not exceed the width of the probed manifold of rotovibrational Raman lines, typically on the order of a few cm\(^{-1}\). This dictates optimum pulsewidths ranging from a few to a few tens of picoseconds for the “stimulating” pulse (which can be either pump or Stokes according to the configuration). The sensing pulse, on the other hand, can have a narrower bandwidth, since its peak power does not affect the SRG/SRL.

In a backward SRS geometry [15] the interaction length is determined by both spatial and temporal properties of the pulses. The spatial interaction length is roughly given by:

\[
L_{\text{spatial}} \approx \min \left( 2z_{Rp}, 2z_{RS} \right)
\]  

(3)

where \( z_{Rp}(z_{RS}) \) is the Rayleigh range of the pump (Stokes) beam. In a backward geometry, the interacting pulses walk through each other, so that the temporal interaction length is approximately given by:

\[
L_{\text{temp}} \approx \frac{1}{2} c \max \left( \Delta t_p, \Delta t_s \right)
\]  

(4)

where \( c \) is the speed of light and \( \Delta t_p(\Delta t_s) \) is the duration of the pump(Stokes) pulse. The temporal interaction length is thus determined by the duration of the longest pulse. The effective interaction length is then given by:

\[
L_{\text{eff}} = \min \left( L_{\text{spatial}}, L_{\text{temp}} \right)
\]  

(5)

In typical focusing conditions for remote sensing, one expects Rayleigh ranges of the interacting beams on the order of tens of centimetres. Therefore, in order to fully exploit the available interaction length, it is necessary that the “probe” pulse has duration of a few nanoseconds. This automatically takes place in our remote sensing scheme, since the atmospheric laser emission has nanosecond pulse duration, as determined by the length of the filament and the lifetime of excited \( \text{N}_2 \) molecules.

From this analysis one can derive the following optimum laser parameters for a remote sensing experiment based on backward SRS:
(i) the backward-propagating atmospheric laser acts as a fixed frequency probe; its energy
is not critical, as long as it can be accurately measured, and its nanosecond duration
supports an interaction length of more than 15 cm;

(ii) the forward-propagating stimulating pulse should be as energetic as possible, its
bandwidth should match typical molecular linewidths in gases and it should be
broadly tunable to address different molecular transitions; focusing of the stimulating
light should be managed to maintain the interaction length.

3. Experimental setup

For our preliminary experiments we employed two different setups, using either ps pump/ps
Stokes or ps pump/ns Stokes pulses, which are shown in Fig. 2. The ps pump/ps Stokes setup
pursuits two purposes. First, it allows relatively easy pre-alignment and optimization of the
spectroscopic setup. Second, as it will be shown further, the results of ps/ps experiments
permit scaling of the expected SRS signals with respect to pulse duration, energy and (or)
spectral width in the case of remote sensing with different laser sources.

Both configurations share a 10 kHz Yb:KGW chirped pulse amplifier (CPA) (Pharos,
Light Conversion) generating 400 µJ, 280 fs pulses centered at 1024 nm fundamental
frequency. The system drives a second-harmonic-pumped optical parametric amplifier (OPA),
producing 40-µJ, 200-fs pulses tunable between 620 and 700 nm. The OPA is seeded by a
white light continuum, generated in a 6-mm long undoped YAG crystal, which is further
amplified in two OPA stages based on 15 mm long Type I lithium triborate (LBO) crystals.
The tunability of the OPA on the short wavelength side is limited by the absorption of the
idler pulses in the LBO crystals. The OPA pulses are sent to a spectral compressor generating
UV pulses (310-350 nm) serving as a tunable Raman pump.

Spectral compression is a simple method for the generation of tunable narrowband
picosecond pulses starting from broadband femtosecond pulses [16, 17]. It is based on a
second-harmonic- generation (SHG) process in the presence of large group -delay-mismatch
(GDM) between the fundamental frequency (FF\text{OPA}) and the second harmonic (SH\text{OPA}) pulses,
which results in a narrow SH bandwidth, given essentially by the inverse of GDM, according
to the formula \( \Delta \nu_{\text{SH}} = 0.886/GDM \) [18], where \( GDM = \delta L_c \), \( L_c \) being the crystal length and
\( \delta = 1/\nu_{\text{FF}} - 1/\nu_{\text{SH}} \) the group velocity mismatch between FF and SH pulses. To achieve large
spectral compression ratios one thus requires long crystals and large values of \( \delta \). For our
wavelength range, the most suited crystal is \( \beta \)-barium borate (BBO) due to its UV
transparency and high damage threshold. Its high spatial walk-off (~2.7°) is not particularly
detrimental for the interaction length thanks to FF\text{OPA} pulses energies of few tens of
microjoules, which enable peak intensities in excess of few GW/cm\(^2\) with quite large beam
diameters, around 1 mm. With a 20-mm-long BBO crystal we obtain UV pulse energies from

Fig. 2. Setups of the proof-of-principle backward SRS experiment with ps pump/ps Stokes (a)
and ps pump/ns Stokes (b).

Spectral compression is a simple method for the generation of tunable narrowband
crystal pulses starting from broadband femtosecond pulses [16, 17]. It is based on a
second-harmonic- generation (SHG) process in the presence of large group -delay-mismatch
(GDM) between the fundamental frequency (FF\text{OPA}) and the second harmonic (SH\text{OPA}) pulses,
which results in a narrow SH bandwidth, given essentially by the inverse of GDM, according
2.5 to 10 µJ in the 310-340 nm wavelength range with linewidths of 30-40 cm\(^{-1}\), as reported in Fig. 3(a). Figure 3(b) shows a sequence of SH spectra obtained by tuning the OPA and simultaneously angle-tuning the BBO SHG crystal. The spectra correspond to the Raman resonances of N\(_2\), O\(_2\) and CH\(_4\) when choosing a Stokes pulse at \(\sim 341\) nm. Since the spectra have been recorded with a spectrometer having spectral resolution of 20 cm\(^{-1}\), the actual linewidths range from \(-22\) to \(-35\) cm\(^{-1}\), which are broader than the expected values (around 10 cm\(^{-1}\) [12]) due to a combination of FF depletion and spatial walk-off in the BBO crystal, which limit the effective interaction length. As an illustration of spectral narrowing and corresponding pulse lengthening, the cross-correlation between the 1024-nm and the UV pulses is given in Fig. 3(c). Deconvolution of the cross-correlation trace reveals a pulse duration of 0.76 ps for the spectrally compressed SH\(_{\text{OPA}}\) of the OPA output. The tunable picosecond pulses obtained in this way are used as Raman pump pulses in both ps/ps and ps/ns configurations.

![Fig. 3. (a) typical spectrum of OPA output (red solid line) and second harmonic (filled area); in order to highlight increased spectral brightness the area under the curves is normalized to pulse energy; (b) spectra of Stokes and pump pulses used in the experiments with picosecond pulses; the area under the curves is normalized to pulse energy; (c) intensity profile of the pulse generated by Yb:KGW CPA system (FF\(_{\text{YB}}\)) and cross-correlation functions between the FF\(_{\text{YB}}\) pulse and spectrally compressed TH\(_{\text{YB}}\) and SH\(_{\text{OPA}}\) pulses.](image)

The experimental configuration of the ps pump/ps Stokes setup is shown in Fig. 2(a). In order to emulate the atmospheric N\(_2\) laser, in this system a fraction of the Yb:KGW laser output, hereafter indicated as FF\(_{\text{YB}}\), is frequency tripled to generate ps Stokes pulses at a fixed wavelength of 341.3 nm. The narrowband third harmonic (TH\(_{\text{YB}}\)) pulses are generated in two steps: first we generate SH\(_{\text{YB}}\) pulses by spectral compression of the FF\(_{\text{YB}}\) in a 20-mm long BBO crystal, and then combine such SH\(_{\text{YB}}\) pulses in a second BBO crystal with the \(\approx 280\)-fs FF\(_{\text{YB}}\) pulses to produce narrow-bandwidth TH\(_{\text{YB}}\) pulses at 341.3 nm. This is achieved with a Type I interaction [FF\(_{\text{YB}}\) (o) + SH\(_{\text{YB}}\) (o) \(\rightarrow\) TH\(_{\text{YB}}\) (e)] in a 10-mm long BBO crystal, such length corresponding to the pulse-splitting length between the SH\(_{\text{YB}}\) and FF\(_{\text{YB}}\) pulse. In such interaction the faster FF\(_{\text{YB}}\) pulse travels through the crystal by superimposing different temporal portions of the slower (and longer) SH\(_{\text{YB}}\) pulse. In a regime of small depletion the...
TH_{YB} pulses result to be transform-limited with nearly rectangular temporal shape. The spectrum of the TH_{YB} pulses, shown in Fig. 3(b), has a FWHM of \( \approx 40 \, \text{cm}^{-1} \) with a pulse duration of 0.6 ps, as extracted from the cross-correlation between TH_{YB} and FF_{YB} shown in Fig. 3(c). The energy of the TH_{YB} pulse is 1 \( \mu \text{J} \), which is comparable to that obtainable in the case of N\_2 lasing from a filament [12].

Pump and Stokes pulses are time-synchronized by a delay line and focused in counter-propagating directions either in air or in a variable-pressure cell filled with the gas sample. Both pump and Stokes beams are focused with 10-cm focal length lenses resulting in waist radii of \( w_{p,s} = 12.5 \, \mu \text{m} \) and in Rayleigh ranges of \( z_{R_p,R_S} = 3.4 \, \text{mm} \), as measured with a beam profiler. The pump pulse is modulated at 375 Hz by a mechanical chopper which also triggers a lock-in amplifier (SR830, Stanford Research). Stokes pulses transmitted through the interaction area are selected by a dichroic mirror and sent to a silicon photodetector. The SRG signal is measured by synchronous detection with a lock-in amplifier. A fraction of the Stokes pulse is sampled before the interaction area to allow for differential detection, which cancels Stokes pulse energy fluctuations and increases the sensitivity.

The experimental configuration of the ps pump/ns Stokes setup is shown in Fig. 2(b). In order to increase the duration of the Stokes pulse and thus the interaction length, so as to better emulate SRS experiments with nanosecond pulses originating from N\_2 lasing in a filament [12], we employ a home-built Q-switched cavity-dumped Nd:YAG laser, electronically synchronized with the Yb:KGW laser. The laser generates 1.2-mJ, sub-10-ns pulses at the repetition rate of 2 kHz, with rms energy stability of 5.5\%. These rather high energy fluctuations are characteristic of Q-switched cavity-dumped lasers where pulse generation starts from noise. The output of the Nd:YAG laser is frequency-tripled by in-line generation of the second harmonic and subsequent sum-frequency-generation with the 1064-nm pulse in 15-mm long Type I and Type II LBO crystals respectively, resulting in 250-\( \mu \text{J} \), 4-ns pulses at 355 nm. In order to increase the spatial beam quality, the 355-nm beam is apertured by a pair of irises, which results in a Stokes pulse energy of 135 \( \mu \text{J} \). The delay between pump and Stokes pulses in the spectroscopic system depicted in Fig. 2(b) is tuned electronically with the precision of 400 ps, which is determined by the time jitter of the cavity-dumped nanosecond pulses. Given the substantially larger energy of the Stokes pulse, we prefer in this setup to detect the SRL signal of the weaker pump. The Stokes is directly modulated dividing by 5 the clock signal derived from the Yb:KGW system and thus running the cavity-dumped Nd:YAG laser at 2 kHz.

4. Results and discussion

We first characterized the ps/ps laser system. To determine the temporal overlap of the pulses, and thus their interaction length in a backward geometry, we performed SRS in a forward geometry. Figure 4(a) shows the SRS signal for atmospheric N\_2 (\( \Omega = 2330 \, \text{cm}^{-1} \)) as a function of the pump-Stokes delay; the signal represents the cross-correlation between the pump and Stokes pulses and has a FWHM of \(-1 \, \text{ps} \). This implies an interaction length of \(-0.15 \, \text{mm} \) in a backward geometry, strongly limiting the SRS signal since much shorter than the spatial overlap length \( L_{\text{spatial}} \) given by the confocal parameter, equal to \( 2z_{R_p,R_S} = 6.8 \, \text{mm} \).

We then performed backward SRS in methane, which has a high Raman cross section \( (d\sigma/d\Omega \approx 38 \times 10^{-35} \, \text{cm}^2/\text{srad}) \) [19,20]. Figure 5(a) shows the SRG spectrum at a pressure of 5 bar around the \( \nu_1 \) band (symmetric CH stretching mode), as acquired by tuning the pump pulse frequency; it peaks around the expected 2915 cm\(^{-1}\). A convolution of the pump and Stokes
spectra with the spectral profile of the 2915-cm\(^{-1}\) Raman line of methane (the solid line in Fig. 5(a)) provides an accurate fit for the experimental spectrum (the dots in Fig. 5(a)). Since the bandwidths of the laser pulses are much broader than the linewidth of the Raman band of methane, this convolution is not sensitive to the specific spectral profile of the Raman band. As expected for SRS, the spectrum does not show any distortion or contribution from non-resonant background.

Figure 5(b) shows the backward SRG signal as a function of the delay between pump and Stokes pulses, both in the temporal (bottom axis) and spatial scales (top axis). Since the spatial overlap between pump and Stokes beams \(L_{\text{spatial}} = 2z_{R_p,RS} = 6.8\) mm is much larger than the temporal pump-Stokes walk-off length \(L_{\text{temp}}\) determined by their pulse widths \(L_{\text{temp}} \approx 0.15\) mm for \(\Delta t_p \approx \Delta t_S \approx 1\) ps, varying the delay time between these pulses is equivalent to scanning the region where these pulses temporally overlap along the pump beam axis (the \(z\)-direction) through the caustics of the pump beam. The maximum signal is thus achieved for a time delay that allows the Stokes pulse to interact with the pump pulse exactly at the pump beam waist. Defining \(z\) as the coordinate measured from the pump beam waist, the results of experiments performed in this regime, as can be seen from Fig. 5(b), are accurately fitted with a standard equation \(\text{SRG}(z) \propto [1 + (z / z_R)]^{-1}\), describing the caustics of a Gaussian pump beam with \(z_R\) being the fitting parameter. The best match with the experimental results was obtained for a \(z_R\) value of 2.6 mm which is in rather good agreement with the experimentally determined Rayleigh range. The \(z\)-coordinate used as the upper abscissa axis in Fig. 5(b) is then mapped onto the delay time \(\Delta t\), shown in the lower abscissa axis, through the \(z = c\Delta t\) transform.

![Fig. 5. (a) SRG spectrum from CH\(_4\) measured in counter-propagating geometry at a 5 bar pressure in ps/ps configuration; (b) dependence of the CH\(_4\) SRG signal on the delay between Stokes and pump pulses; experiments are done in counter-propagating geometry in ps/ps configuration; dots represent experimental points, solid lines are the results of calculations.](image-url)
Figure 6 shows the SRG signal as a function of methane pressure, highlighting the linear concentration dependence that is characteristic of SRS. This is verified by the calculations shown by the solid line in Fig. 6(a), performed by solving nonlinear coupled equations for slowly varying envelopes of the pump and probe (Stokes in the SRG scheme or pump in the SRL scheme) pulses, in the plane wave limit. It was possible to detect the SRG signal for pressures down to 40 mbar. In such conditions the SRG signal reaches a value of $10^{-5}$, which corresponds to the noise floor of the setup with an integration time of 1 s.

Figure 4(b) shows the backward SRS signal in atmospheric conditions for oxygen and nitrogen when tuning the system to 1555 and 2030 cm$^{-1}$, respectively. As expected, the behavior of the SRG signal as a function of the time delay between pump and Stokes pulses follows that obtained with methane. Predictions from the caustics model (solid line in Fig. 4(b)) closely follow the experimental data (dots in Fig. 4(b)). In both cases the SRG signal is at the $10^{-5}$ level, thus far from concrete application perspectives, mostly due to the extremely short interaction length, to the limited energy of the pump pulses and to the non-optimum pulse bandwidth.

The ps/ns system, despite the added complexity of synchronization of two lasers, alleviates these drawbacks by significantly increasing the interaction length, up to the nearly 7 mm value dictated by $L_{\text{spatial}}$, and decreasing the spectral width of the Stokes pulse. Figure 7 shows the SRL signal obtained when tuning the pump/Stokes frequency difference around the methane resonance at a pressure of 5 bar. The spectral response is narrowed by nearly a factor of 2 with respect to that reported in Fig. 4(a), and its 17 cm$^{-1}$ FWHM remains limited, as confirmed by our simulations (the solid line in Fig. 7), by the bandwidth of ps pump pulses. When comparing the SRS values at the resonance, a value of $\sim 2 \times 10^{-3}$ is found for the ps/ns configuration, which is 2.5 times smaller than in the ps/ps configuration. Such scaling is in good agreement with the discussion given in Section 2, where the SRS signal was shown to be proportional to the peak intensity of the driving field and to the interaction length. If a correction factor given by the ratio of the ns and ps pulse bandwidths is added to the scaling law to account for the different spectral overlap with the Raman band, the expected SRS ratio reads:

$$\frac{\text{SRS}_{\text{ns}}}{\text{SRS}_{\text{ps}}} \propto \frac{L_{\text{ns}} L_{\text{ps}} B_{\text{ps}}}{L_{\text{ps}} L_{\text{ns}} B_{\text{ns}}} \propto \frac{U_{\text{ns}} L_{\text{ns}} B_{\text{ps}} \Delta t_{\text{ps}}}{U_{\text{ps}} L_{\text{ps}} B_{\text{ns}} \Delta t_{\text{ns}}} = 1.2$$

where $U$ is the stimulating pulse energy (135 µJ and 4 µJ for ns and ps experiments, respectively) and $B$ the pulse bandwidth (9 and 33 cm$^{-1}$ in the two cases). The discrepancy with the experimental result mostly derives from the reduced spatial overlap of the Stokes and
pump beams. The output of the nanosecond Nd:YAG laser is highly multimode, leading to substantially worse focusability of the Stokes beam (we have measured $2\zeta_{\text{phot}} = 0.5$ mm which is more than 10 times smaller as compared to the frequency doubled output of the OPA); this is expected to decrease the spatial overlap between the nanosecond Stokes and picosecond pump beams which will substantially influence last two terms in the Eq. (6).

5. Outlook and conclusions

The results of this study allow to extrapolate the laser parameters required for a true standoff sensing based on backward SRS from an atmospheric laser and to design a system accordingly. Lasing in nitrogen has been proven to be more efficient when driven by mid-infrared pulses at 3.9 µm [12], because the longer driving wavelengths allow for higher ponderomotive energies of the electrons, and thus for a more efficient pumping of nitrogen into its excited electronic states. In future work, we plan to generate intense 3.9 µm pulses [21] and synchronize them with tunable picosecond UV pulses with $\approx 5$-mJ energy to be used as a pump for standoff SRS.

We are now in a position to use the results of our model experiments to estimate the performance attainable in a standoff detection arrangement using a forward UV pump, provided by a ground-based laser as above specified, and a backward probe from a filamentation-assisted nitrogen laser in the atmosphere. In the regime of interest, the SRG/SRL signal scales with the product $G = gI_pL_{\text{eff}}$, where $g \propto d\sigma/d\Omega$ is the Raman gain coefficient, $I_p$ is the intensity of the pump pulse and $L_{\text{eff}}$ is the effective interaction length. As shown in the earlier work [12], a filamentation-assisted N$_2$ laser in the atmosphere delivers coherent UV pulses at 337 nm with a typical pulse width of $\approx 1$ ns. With pump pulses of duration $\Delta\tau_p \approx 20$ ps and Stokes pulses with $\Delta\tau_S \approx 1$ ns, the temporal walk-off length of the pump and probe pulses is estimated as $L_{\text{temp}} \approx 15$ cm. This large walk-off length is highly favorable for the standoff detection mode as it allows a strong enhancement of the SRS signal and enables the remote sensing of the atmosphere using loosely focused light beams. In particular, an on-ground focusing element with a focal length of 1 km will focus a laser beam with a wavelength of 350 nm and an initial radius of 1.22 m into a beam-waist radius $w_0 \approx 90$ µm, which corresponds to a confocal parameter $b \approx L_{\text{temp}}$ for the considered backward SRG/SRL scheme. In such conditions the enhancement in the SRG/SRL signal with respect to the above described ps/ps experiment can be quantified in terms of a factor $\eta$, defined as
\[ \eta = \frac{SRS_{\text{opt}}}{SRS_{\mu}}, \text{ SRS}_{\text{opt}} \text{ being the signal measured under standoff detection conditions with the} \]

optimized 5-mJ UV pump laser described above. As specific examples, we consider SRS-based standoff detection of carbon monoxide, sulfur dioxide, nitrogen dioxide, and ammonia, known as significant factors of air pollution, as well as of N\textsubscript{2} and O\textsubscript{2}. By taking into account their known Raman scattering cross sections [22–24], the following values for \( \eta \) are found: \( \eta_{\text{N}_2} \approx 370, \ \eta_{\text{O}_2} \approx 407, \ \eta_{\text{CO}} \approx 310, \ \eta_{\text{SO}_2} \approx 830, \ \eta_{\text{NO}_2} \approx 90, \ \eta_{\text{NH}_3} \approx 1300, \) corresponding to an average sensitivity enhancement of two orders of magnitude.

In conclusion, this work provides a detailed feasibility study of an ambitious standoff detection scheme for gaseous chemicals based on backward SRS in combination with filamentation-assisted lasing in atmosphere. Preliminary results obtained at a laboratory level demonstrate the technical viability of the approach and allow to extrapolate the laser parameters required for a real standoff atmospheric experiment.

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