Transient stimulated Raman scattering in gas mixtures

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We studied, for the first time to our knowledge, transient stimulated Raman scattering in H_2-D_2 and H_2-CH_4 gas mixtures excited with 200-fs and 2-ps, 390-nm pulses. Depending on the composition and partial pressure, of those gases, we observed ~40 output lines simultaneously. Under optimum conditions a conversion efficiency of as much as 8% in the combination Raman line at 556 nm was obtained in the H_2-CH_4 gas mixtures. The difference between picosecond and femtosecond pumping is due to self-phase modulation and to generation of a spectral continuum in the latter. Our calculation of the ratio of the partial pressures is in a good agreement with the experimental results. A new method for measuring the unknown Raman scattering cross section of gas molecules is suggested.   © 1999 Optical Society of America

OCIS codes: 190.5650, 190.7110, 190.2620, 190.5890.

Stimulated Raman scattering (SRS) is a well-known method for frequency conversion of laser radiation ranging from the UV to the IR.[1]   SRS is successfully used for both continuous-wave lasers[2] and nanosecond, picosecond, and femtosecond pulsed lasers.[3-8]

Pressurized molecular gases such as hydrogen, deuterium, and methane appear to be the most suitable Raman-active media for frequency conversion of intense ultrashort pulses.[4-8]   These gases possess several properties that make them especially suitable for frequency conversion, including large rotational and vibrational Stokes frequency shifts, a high degree of optical homogeneity, and relatively low group-velocity dispersion for ultrashort pulses. In addition, these gases are photochemically stable, and one can vary their optical and spectroscopic parameters by changing the pressure.

In previous investigations of nanosecond SRS in the dual gas mixtures H_2-CH_4 and H_2-D_2,[9-14] additional combination lines were observed at the sum and difference frequencies of Stokes and anti-Stokes spectral components of the individual gases according to

$$\nu = \nu_L + i\nu_{V1} + j\nu_{R1} + m\nu_{V2} + n\nu_{R2}$$

$$(i, j, m, n = 0, \pm 1, \pm 2, \ldots), \quad (1)$$

where ν_L is the frequency of the pump laser and $\nu_{V1,R1}$ and $\nu_{V2,R2}$ are the Raman vibrational and rotational frequency shifts for the components of gas mixture.

In Refs. 6–8 it was shown that, in gases such as H_2, D_2, HD, and CH_4, transient SRS can result in the efficient conversion of 400-nm radiation into more than 40 Stokes and anti-Stokes lines ranging from the UV to the near IR, defined by the molecules' vibrational and rotational frequencies. The important role of competing nonlinear processes such as white-light generation that limit the ultimate conversion efficiency of SRS was established for pump pulses of <1 ps. Therefore it is important to investigate the characteristics of transient SRS with pump pulses of both picosecond and femtosecond duration.

We report, for the first time to the best of our knowledge, the transient SRS generation of combination frequencies in dual mixtures of Raman-active gases H_2-CH_4 and H_2-D_2 with pump pulses of 200-fs and 2-ps duration. We demonstrate the efficient generation of combination lines in gas mixtures excited by 2-ps pulses. Self-phase modulation and white-light generation limit the ultimate conversion efficiency for 200-fs pump pulses on all Raman lines and especially on the combination lines.

Transient SRS occurs when the duration of the pump pulse τ_p is much shorter than the vibrational and rotational dephasing time T_2 of the gas molecules, $\tau_p < T_2$. In this case the intensity of the Stokes beam at the output of the medium can be approximately expressed as[8,15]

$$I_S = I_0 \exp\left[\frac{8g}{T_2} \int_0^L \int_0^{\tau_p} I_p(z,t)\mathrm{d}z\mathrm{d}t \right]^{1/2}, \quad (2)$$

where I_p is the intensity of the pump pulse, I_0 is the initial Stokes intensity, g is the steady-state gain coefficient, and z is the interaction length.

In the experiments with nanosecond SRS in gas mixtures,[11-13] the authors observed the maximum energy in the combination Stokes lines $I_{-1-1} = \max [i = m = -1, j = n = 0;$ Eq. (1)] when the intensities of the first Stokes components of both gases were equal, $I_{0-1} = I_{-10}$. As I_p is the same for both components of the gas mixture, we can obtain the condition of optimal

conversion into the combination lines, using Eq. (2), as

$$\frac{g^{(1)}}{T_2^{(1)}} = \frac{g^{(2)}}{T_2^{(2)}} . \tag{3}$$

For the first Stokes component, the steady-state gain coefficient g in gases can be expressed as

$$g = \frac{2\lambda_S{}^3 T_2 \Delta N}{hc} \frac{d\sigma}{d\Omega} , \tag{4}$$

where ΔN is the vibrational (rotational) population difference between the initial and the final states of the Raman-active molecule, λ_S is the Stokes wavelength, $\partial\sigma/\partial\Omega$ is a Raman differential scattering cross section, h is Planck's constant, and c is the speed of light in vacuum.

Taking into account that $\Delta N = FN \sim Fp$, where N is the total density of the gas molecules, p is the partial gas pressure, and F is the Boltzmann population factor, we can derive from Eqs. (3) and (4) that the optimum ratio R for the two components is

$$\frac{p^1}{p^2} = \frac{F^2(\lambda_s{}^2)^3}{F^1(\lambda_s{}^1)^3} \frac{\left(\frac{\partial\sigma}{\partial\Omega}\right)^2}{\left(\frac{\partial\sigma}{\partial\Omega}\right)^1} = R . \tag{5}$$

Equation (5) shows that for transient SRS the ratio of optimal partial gas pressures R for the efficient generation of the combination Raman lines is inversely proportional to the ratio of Raman differential scattering cross sections, the cube of the Stokes wavelengths ratio, and the ratio of Boltzmann factors.

The parameters used in Eq. (5) for the gases investigated at a pump wavelength $\lambda_P = 400$ nm are shown in Table 1. From the data given in Table 1 we calculate that the optimum ratio for the H_2-D_2 mixture is $R = 0.385$ and for the H_2-CH_4 mixtures is $R = 3.4$.

In our experiments we used two different regeneratively amplified Ti:sapphire laser systems: TSA-50 (Positive Light), generating 2-ps pulses at the second-harmonic wavelength 400 nm with pulse energies of 4 mJ at a 10-Hz repetition rate, and CPA-1000 (Clark-MXR), generating 200-fs pulses at the second-harmonic wavelength 390 nm with pulse energies of 0.3 mJ at a 1-kHz repetition rate. A 100-cm-long stainless-steel cylinder with 25-mm-diameter quartz windows served as the Raman cell. The partial gas pressures were varied from 2 to 48 atm, with the total pressure kept constant at 50 atm. Under these conditions the characteristic vibrational dephasing times T_2 for H_2, D_2, and CH_4 molecules are 100, 50, and 10 ps, respectively.[8] As these relaxation times are longer than the duration of the excitation pulses, all our experiments were performed in the transient regime of the stimulated Raman process. Two lenses with a focal length of 1 m were used to focus the input beam into the Raman cell and to collimate the output beam. We measured the energy and the spectrum of the generated pulses by splitting the beams between an optical powermeter and a grating spectrometer.

At the first stage of the experimental study we determined the optimum partial pressures in the gas

mixtures H_2-CH_4 and H_2-D_2. Experimentally we changed the partial pressure in the mixtures and measured the output energy in both first Stokes lines, I_{0-1}, and I_{-10}, as well as the combination line I_{-1-1}. As already has been observed,[14] the maximum efficiency in the combination lines was achieved when the output Stokes energies were the same in both lines I_{0-1} and I_{-10}. For the combination line I_{-1-1} we obtained high conversion efficiency; other combination lines had a considerably lower SRS efficiency. The $\nu_{-1,-1}$ combination lines were shifted by 7142 cm^{-1} in H_2-D_2 and by 7072 cm^{-1} in H_2-CH_4, corresponding to wavelengths at 559 and 557 nm, respectively.

Figure 1 shows the measured dependence of the energy in the $\nu_{-1,-1}$ combination line on the partial pressure of H_2 in H_2-CH_4 and H_2-D_2 gas mixtures for 2-ps pump pulses with an energy of 3 mJ. According to the maxima in Fig. 1, we determined the ratio of partial pressures that correspond to the highest conversion efficiency. The experimental values obtained were $R \approx 14/36 (\pm 0.5$ atm$) \approx 0.39 (\pm 0.02)$ for H_2-D_2 and $R \approx 38/12 (\pm 0.5$ atm$) \approx 3.17 (\pm 0.18)$ for H_2-CH_4. The results are in good agreement with our calculation in Eq. (5). Hence one can use the measurements of the optimal partial pressure for the determination of the unknown Raman cross section of a gas by using transient SRS in mixtures of this gas with H_2 or CH_4.

For 200-fs pump pulses the combination line $\nu_{-1,-1}$ at 557 nm was observed only in H_2-CH_4 gas mixtures, with an optimal partial pressure ratio of 40/10, close to the result obtained with 2-ps pump pulses. The SRS process was less efficient because of competition with white-light generation. In the H_2-D_2 gas mixtures the strong background that was due to white-light

Table 1. Parameters of the Investigated Gases

Gas	ν_V (cm^{-1})[a]	F^a	λ_S (nm)	$\dfrac{\partial\sigma}{\partial\Omega} / \dfrac{\sigma\partial}{\partial\Omega} (H_2)^b$
H_2	4155	0.66	480	1
D_2	2987	0.38	454	0.79
CH_4	2917	1	452	2.7

[a]Ref. 16.
[b]Ref. 17.
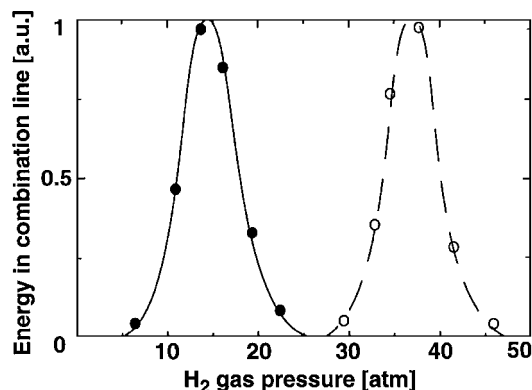

Fig. 1. Dependence of the energy in the combination line on the partial pressure of H_2: solid curve, $H_2 + D_2$ gas mixture; dashed curve, $H_2 + CH_4$ gas mixture.
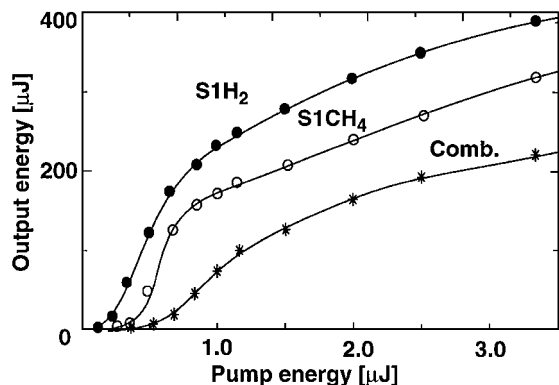
Fig. 2. Dependence of the energy of several SRS output components on the energy of the pump pulse. Filled circles, first Stokes of H_2, I_{-10}; open circles, first Stokes of CH_4, I_{0-1}; stars, combination line, I_{-1-1}. Partial pressures of 38 atm of H_2 and 12 atm of CH_4 were employed.

generation completely prevented the observation of the combination line. Also, for 200-fs pump pulses white-light generation limited the ultimate conversion efficiency at all Raman lines. The small efficiency of femtosecond SRS in gas mixtures is a peculiar feature of the process because, in pure H_2, D_2, or CH_4, femtosecond SRS is highly efficient.[5-8]

Figure 2 shows the energies of the first Stokes lines (480 nm for H_2, 453 nm for CH_4) and of the combination line (557 nm) as functions of pump-pulse energy in a H_2−CH_4 gas mixture. The pump-pulse duration was 2 ps, and the partial pressure was close to the optimum, 38/12 atm.   For the combination line a conversion efficiency of as much as 8% was measured. To increase the output energy efficiency in line I_{-1-1} one should make the Stokes components I_{0-1} and I_{-10} equal with maximum accuracy, because in our experiments we observed a strong dependence of the energy in the combination line on the partial pressure of the gases (see Fig. 1).   Additionally, Fig. 2 shows a very high total SRS conversion of ~30% for all three components.

At the optimum partial pressure of the gas mixtures we also measured the spectra of the SRS output from the UV to the near IR. We observed more than 40 different Raman lines: vibrational as well as rotational and vibrational–rotational, with frequencies that can be determined from Eq. (1).

In conclusion, we have investigated the efficiency and spectral characteristics of SRS in the femtosecond and picosecond time domains in two gas mixtures, H_2−D_2 and H_2−CH_4. The optimal conditions for efficient generation of combination lines were determined theoretically and experimentally. A conversion efficiency into the combination line at 557 nm of as much as 8% was achieved. With 2-ps pump pulses SRS in gas mixtures was demonstrated to be an efficient method for simultaneous generation of many spectral

lines from the UV to the near IR. For 200-fs pump pulses white-light generation limited the ultimate conversion efficiency at all Raman lines and especially at the combination lines. Our theoretical calculations of the optimum ratios of partial pressures for transient SRS, which are inversely proportional to the Raman cross sections, are in good agreement with the experimental results. The measurements of optimal ratio of partial gas pressures can be used for the determination of unknown Raman cross section of a gas by use of transient SRS in a mixture of this gas with H_2 (or CH_4). These experimental data on unknown Raman scattering cross sections might be useful for high-sensitivity remote pulsed Raman spectroscopy of gaseous atmospheric pollutants.

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