Relative Intensity Distribution of the Stimulated Raman Scattered (SRS) Lines of Methane and Hydrogen Excited with 266 nm UV Radiation

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The stimulated Raman Spectrum (SRS) due to the Raman active symmetric stretching modes (ν_1) of vibration of both hydrogen and methane were recorded and a comparative study of their relative intensities as well as the wavelength conversion efficiencies were carried out. It was found that hydrogen showed much higher wavelength conversion efficiency than methane due the seeding of third SRS line at 397.8 into Balmer H-ε line at 397 nm in hydrogen. The input pulse energy dependence on the SRS signal showed a linear dependence for methane and a non linear dependence for hydrogen.

Keywords: Stimulated Raman scattering (SRS), hydrogen, nonlinear phenomenon, seeding and amplification, UV sources, tunable coherent sources, Raman frequency shifting.

1   Introduction

Methane and hydrogen are the molecules on which Stimulated Raman Scattering (SRS) was first observed in the gas phase and owing to their simplicity, these two molecules remain to be the good candidates for SRS studies. Most of the previous works on SRS in hydrogen [1-6] and methane [5-6] were carried out in the infra red and visible region. Tomov *et al.* [7] observed the enhancement of the first Stokes line in hydrogen and methane excited by 193 nm picosecond laser. In the case of hydrogen, Haner *et al.* [8] estimated the conversion efficiency of only the normal SRS first and second Stokes lines of hydrogen with the excitation of 266 nm.

The Stimulated Raman Scattering (SRS) process is based on the parametric coupling of laser waves, Stokes wave and optical phonon [9, 10]. SRS is a secondary phenomenon in which the normal Stokes/Anti Stokes radiations ($\breve{\nu}_n = \breve{\nu}_0 \pm n\breve{\nu}_i$) are inverted in population

by the interaction of intense laser beam. The following equation describes the probability (P) for the absorption of incident radiation and emission of stokes and anti stoke lines in the SRS process

$$P = \frac{16\pi^4}{h^4} \int |R^{pq}|^2 \, \rho_0 (8\pi \breve{\nu}_n^3 + \rho_n) c d\breve{\nu}_0. \tag{1.1}$$

In the expression (1.1) ρ_0 and ρ_n are the radiation densities of the excitation frequency (ν_0) and the Raman scattering frequency (ν_n) corresponds to a particular vibrational mode respectively and R^{pq} is the transition moment for the two photon process in going from state p to state q through a virtual state. The first term in the equation contributes to the spontaneous Raman scattering, while, $\rho_0 \rho_n$ in the second term contributes to the stimulated phenomenon. Unless a strong laser beam is applied the second term is too small for the stimulated effect to be present.

This paper mainly aims at a comparative study between methane and hydrogen in terms of their relative intensity distribution of the Stimulated Raman Spectra and the wavelength conversion efficiency when excited with 266 nm UV radiation. The SRS spectrum of methane showed the normal intensity distribution expected in the SRS spectrum, where as hydrogen showed a huge deviation from the normal behavior. Particularly, the third Stokes lines of hydrogen ($\breve{\nu}_3 = \breve{\nu}_0 - 3\breve{\nu}_1$) at 397.8 nm, showed an abnormal conversion due to seeding of self excited of H-ε Balmer line at 397 nm into the above SRS line. The excitation energy of 266 nm is above the dissociation energy of hydrogen molecule and hence there is an atomic emission in conjunction with the SRS scattering takes place and consequently atomic lines are emitted and the weak Balmer H-ε line at 397 nm coincides the wavelength of the third stokes line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\breve{\nu}_1$) at 397.8 nm resulting in the enhancement of the SRS intensity. Also in this work, we studied the conversion efficiencies of all the stokes lines of both methane and hydrogen and we noticed that the third Stokes SRS line at 397.8 nm stands out and showed a completely different behavior.

2   Experimental Set Up

The excitation source of 266 nm UV radiation was generated by the fourth harmonic of the pulsed Nd: YAG (Spectra Physics Model GCR-250 - Repetition rate 10 Hz, pulse width 9 ns) with non linear crystals. A beam splitter / power meter arrangement is used to monitor the stability of the laser pulse energy through out the experiment and the laser system was found to be remarkably stable. A proper filter is used to cut off other harmonics of the laser other then 266 nm The experimental cell is 1 meter long stainless steel chamber with high quality quartz windows to withstand high UV power. The cell is a tight vacuum and has the provision for monitoring pressure and temperature and the high vacuum is always maintained in the cell to avoid all kind of contamination. A 50 cm focal length quartz lens was employed to focus the laser beam at the centre of the cell. The Hydrogen and methane

used for this study is of high purity (99.99%).

The SRS signal and the residual laser beam is collected by a UV grade collimating lens and multimode sampling fiber with SMA connector and is transferred to LIB2000 Spectrometer (Ocean Optics). The LIBS 2000 has four spectrometer modules to provide high resolution (FWHM = 0.1 nm) in the 200 nm to 620 nm wavelength region. The detector has a gated CCD camera having 14,336 pixels and this makes it possible to measure a wide wavelength range (200 - 620 nm). The spectrometer is calibrated to the pulse energy using energy meter (Ophir Model 300). All the SRS spectra were recorded with an average of 50 laser shots to avoid any fluctuations in laser output energy.
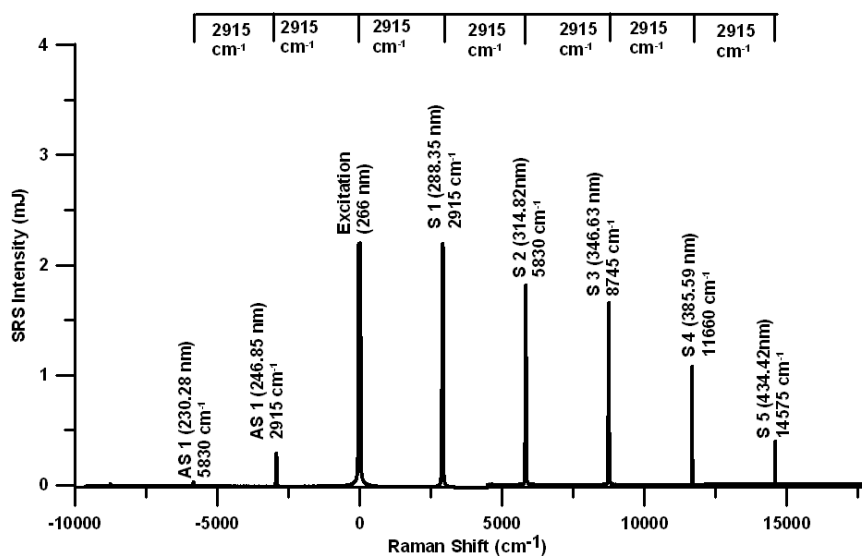
3   Results and Discussions

Figure 3.1: The Stimulated Raman Spectrum (SRS) of methane excited with 266 nm. The pulse energy was 22 mJ and the cell pressure was 5 bar.

Figure 3.1 is the Stimulated Raman Spectrum (SRS) of methane excited with 266 nm laser with a pulse energy of 22 mJ and a cell pressure of 5 bar. A series of equally spaced Stokes and anti Stokes lines are marked on the spectrum with emitted wavelengths listed in the bracket. All the Stokes ($\breve{\nu}_n = \breve{\nu}_0 - n\breve{\nu}_1$) and anti stokes lines ($\breve{\nu}_n = \breve{\nu}_0 + n\breve{\nu}_1$) have recorded an energy separation of 2915 cm-1 between any two neighboring lines, which accounts for the symmetric stretching mode n_1 of methane molecule [11-13]. The relative intensities are presented in terms of actual measured output energies of individual SRS lines. The SRS of methane at 266 nm excitation is quite different from the one reported with 355 nm excitation [14], that in the latter case both symmetric stretching n_1 as well as

bending mode ν_2 of vibrations are excited and in the former case only ν_1 mode is active, no matter how high we raise the laser pulse energy and cell pressure. Another difference we notice in the 266 nm excitation is the measurable intensities of two anti Stokes lines which were either too weak to measure or not at all present in the case of 355 nm excitation of methane. The relative intensities of all the Stokes lines ($\breve{\nu}_n = \breve{\nu}_0 - n\breve{\nu}_1$), starting from $n = 1$ to $n = 5$ are all recorded with reducing intensities which is quite expected in the case of SRS spectrum.

In the SRS phenomenon, the pump energy takes the molecule to a first virtual state bringing about the first Stokes scattering ($\breve{\nu}_1 = \breve{\nu}_0 - 1\nu_1$). This ($\breve{\nu}_1 = \breve{\nu}_0 - 1\nu_1$) radiation would further take the molecule to the second virtual state resulting in the scattering of the second Stokes line ($\breve{\nu}_2 = \breve{\nu}_0 - 2\nu_1$), then the radiation of the second Stokes line would promote the molecule to the third virtual state and subsequent scattering of the third Stokes line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\nu_1$) and so on and this would result in the intensity to fall with the decreasing order of SRS lines. The same mechanism is true in the case of anti Stokes lines ($\breve{\nu}_n = \breve{\nu}_0 + n\breve{\nu}_1$), with the lines with higher n diminish in intensity. This behavior of diminishing intensity of SRS line with increasing order could be understood with the above discussion in conjunction with equation 1. Generally as the order increases, the incident radiation density ρ_0 will be the stokes intensity of the previous line (i.e lower order) and hence it is clear that the intensities of SRS lines will diminish with increasing order [15].

Figure 3.2 depicts the stimulated Raman spectrum (SRS) due to the symmetric stretching mode ν_1 of molecular hydrogen. The spectrum was taken with the excitation of 266 nm UV laser beam at 22 mJ pulse energy and with the cell pressure of 5 bar of H_2. The spectrum shows a set of five Stokes ($\breve{\nu}_n = \breve{\nu}_0 - n\nu_1$) and two anti stokes lines.

($\breve{\nu}_n = \breve{\nu}_0 + n\nu_1$), separated one another by approximately 4156 cm-1, which is the characteristic wave number of the symmetric stretching mode of hydrogen. This is the only vibrational mode of hydrogen, which is Raman active and infra red inactive. The relative intensities are presented in terms of actual measured output pulse energies of individual SRS lines and actual recorded wavelength of each line is presented within the parenthesis as in the case of methane. Figure 3.2, is quite similar to a SRS spectrum of any excitation wavelength in terms of the Raman shift of each line reported in open literature [2, 8, 16].

However, we observe the relative intensities of the SRS lines of hydrogen excited with 266 nm considerably deviates from the usual diminishing intensity pattern inherent to SRS spectrum due to the mechanism described earlier and like the one we presented in Figure 3.1 for methane. Also if we compare the overall intensities of the spectrum presented in Figure 3.1 for methane and Figure 3.2 for hydrogen, the latter spectrum is in general more intense than the one in the former case. The major striking difference in the relative intensity distribution of the hydrogen SRS spectrum excited with 266 nm is the abnormal intensity builds up of third Stokes line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\breve{\nu}_1$) at 397.8 nm. This unusual intensity build up for a particular line is not possible just with the SRS mechanism.
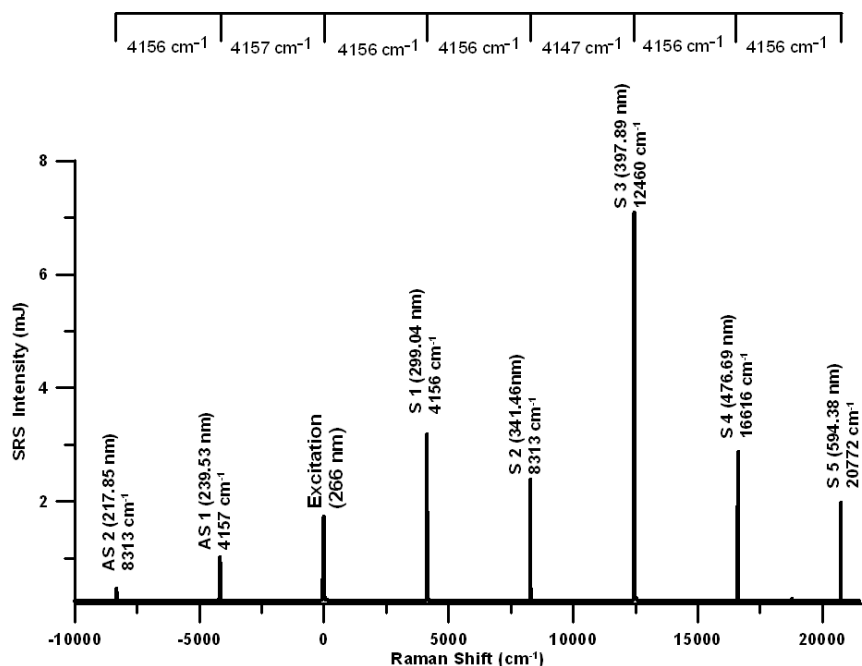
Figure 3.2: The Stimulated Raman Spectrum (SRS) of hydrogen excited with 266 nm. The pulse energy was 22 mJ and the cell pressure was 5 bar.

This drastic intensity deviation could arise due to the close proximity of H-ε Balmer line at 397 nm and the third Stokes line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\nu_1$)at 397.8 nm of H_2 . As the 266 nm is higher than the dissociation energy of the hydrogen molecule which is 36118 cm-1 (276.87 nm), there will be generation of atomic hydrogen and H-ε Balmer line In the case of hydrogen- 266 nm SRS spectrum, H2 molecule in the third virtual state is in resonance with the Balmer line at 397.0 nm and hence the seeding of spontaneous Balmer line in the population inverted system takes place and brings about the drastic enhancement of intensity for the of the third SRS line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\nu_1$) at 397.8 nm [17].

We can notice that the third Stokes line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\nu_1$) at 397.8 nm is a little bit far from the Balmer line at 397.0 nm. However, considering the 0.3 nm line width of the SRS lines and the typical broadening and shifting of the Balmer lines with experimental condition [18] can account for the small difference of about 0.8 nm. Besides the abnormality on the third Stokes line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\nu_1$) at 397.8 nm, the fourth ($\breve{\nu}_4 = \breve{\nu}_0 - 4\nu_1$)Stokes line at 477 nm also shows a little bit of deviation from the normal trend described in the previous paragraph. The nearest Balmer line to this Stokes line is the H-β. Balmer line around 486 nm which is around 9 nm away from the fourth Stokes line, which is quite far compared to the 0.8 nm separation between third Stokes line and H-ε Balmer line. However the intensity of the H-β Balmer line is 10 fold stronger than the H-ε Balmer line [18] and this

Table 1: The conversion efficiency of the SRS lines of hydrogen and methane excited with 266 nm at 22 mJ laser pulse energy

Lines	Hydrogen		Methane	
	Wavelength (nm)	Percentage of gain (%)	Wavelength (nm)	Percentage of gain (%)
Stokes 1	299.04	14.5	288.35	10
Stokes 2	341.46	10.9	314.82	8
Stokes 3	397.89	36	346.63	7.2
Stokes 4	476.69	12.7	385.59	4.5
Stokes 5	594.38	9	434.42	1.8
Anti Stokes 1	217.85	7.72	246.85	1.3
Anti Stokes 2	239.53	4	230.28	0
Total (%)		88.9		32.8

could have contributed to the minor deviation for the fourth Stokes line from the normal SRS spectrum.

In the above two SRS spectra, the input or the excitation wavelength of 266 nm is converted into a new set of wavelengths, which, in principle can be separated and put into use. The conversion efficiency of each wavelength of both methane and hydrogen for the excitation pulse energy of 22 mJ are listed in table 1. In the case of methane the efficiency of the first Stokes line is 10 % and the conversion efficiency of all the subsequent lines are in a decreasing order, which is quite natural as far as the SRS spectra is concerned. In the case of hydrogen, the first stokes line ($\breve{\nu}_1 = \breve{\nu}_0 - 1\nu_1$) starts with 14.5 and generally decreases for the subsequent lines except for the third Stokes line ($\breve{\nu}_3 = \breve{\nu}_0 - 3\nu_1$) at 397.89 nm, which shows an enormous conversion efficiency. If we take the total conversion efficiency of all the SRS lines and compare both methane and hydrogen, we can notice that the conversion efficiency of hydrogen is almost three fold greater than that of methane. Even if we exclude the 36 % conversion efficiency of third SRS line of hydrogen, the other lines of hydrogen show still higher conversion efficiency than that of methane.

In order to understand the seeding mechanism involved in the third SRS line of hydrogen, we carried out a study for the evolution of these line with the excitation pulse energy. Figure 3.3 shows the pulse energy dependence of one representative Stokes line from both
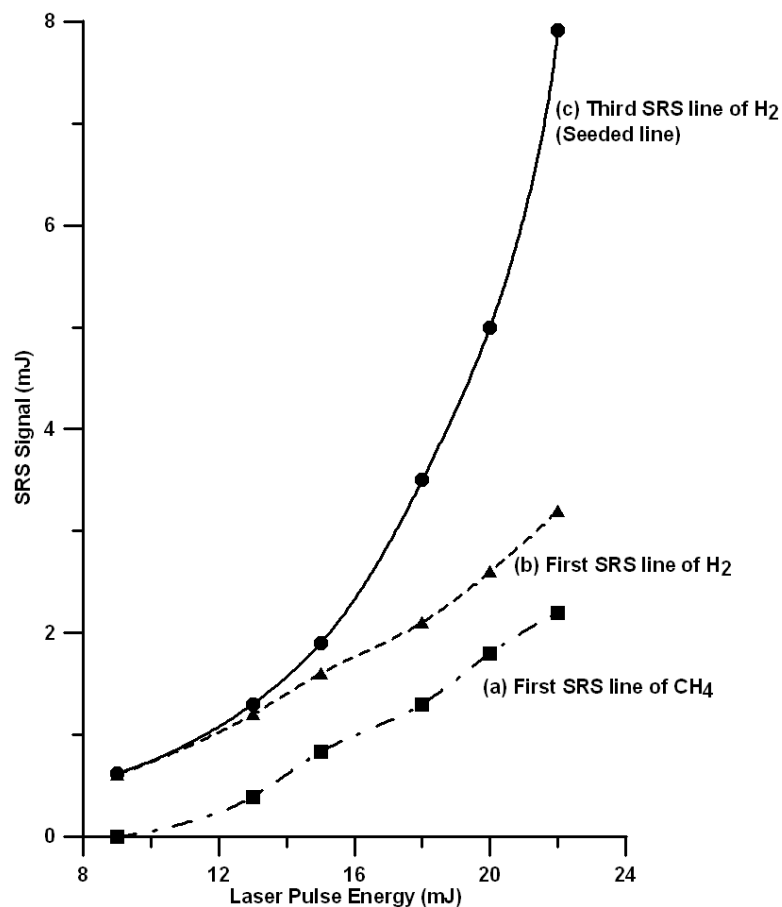
Figure 3.3: The laser pulse energy dependence of SRS signal calibrated to the pulse energy for (a) first stokes line of methane (b) first stokes line of hydrogen (c) Third stokes line of hydrogen excited with 266 nm.

hydrogen and methane, in addition to the seeded SRS line of hydrogen (third Stokes line). The representative lines of both hydrogen and methane are the first Stokes line, as they are the highest but for the seeded line in the case of hydrogen. The cell pressure was kept at 5 bar and the laser pulse energy was varied between 9 to 22 mJ in all three cases. It is well known that in the case of SRS lines even without seeding, the intensity should show a slope of greater than one which is obvious for the non seeded lines of methane and hydrogen [14]. When it gets seeded this non linear behavior drastically increases with much higher slope which is evident in Figure 3.3. At lower laser pulse energies up to 13 mJ, all the three lines show less nonlinear trend and above 13 mJ the third Stokes line of hydrogen starts to deviate substantially from the first SRS lines (non seeded SRS lines) of hydrogen and methane and finally at the pulse energy of 22 mJ, the output energy becomes almost 3 times
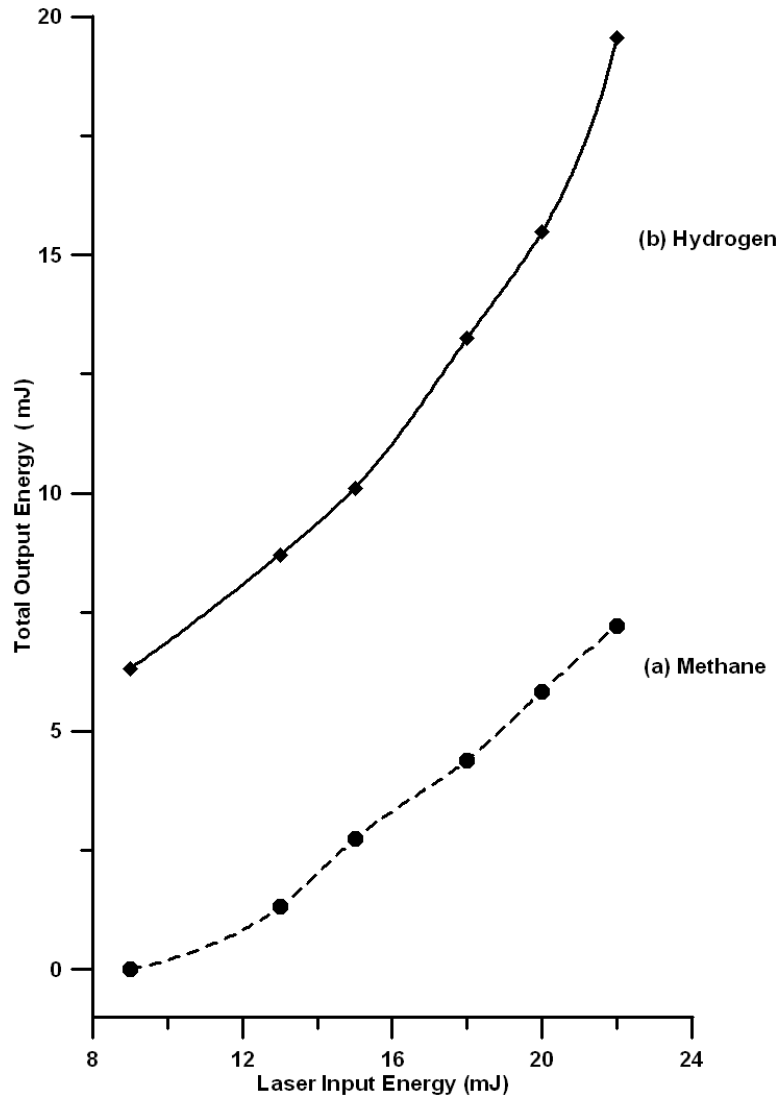
Figure 3.4: The input pulse energy dependence of total output energy of all the recorded SRS lines for (a) methane and (b) hydrogen excited with 266 nm.

more than the other two SRS lines of methane and hydrogen. This indicates that until the laser pulse energy reaches the threshold of around 13 mJ, the seeded SRS line behaves like any other SRS lines due to the absence of atomic emission and at the pulse energy of 13 mJ, the dissociation takes place and the process of seeding sets in. Now the degree of non linearity of energy dependence trend is different because the line at 397.8 nm is subjected to the combined effect of both normal stimulated Raman as well as the seeding process.

We calculated the total output energies of all the lines for both the gases in order to

compare the wavelength conversion efficiencies of both methane and hydrogen. Figure 3.4 depicts thee total output energies of hydrogen and methane for the excitation pulse energy ranging from 9 mJ to 22 mJ. Here also the cell pressure was kept at 5 bar. From Figure 3.4, it is quite clear that the output energy of hydrogen is higher than that of methane even if the enhancement due to seeding process is not considered. When the seeding process sets in, of course the output energy of hydrogen becomes much higher. Methane retains its linear behavior even when all the SRS lines are taken together, where as hydrogen exhibits the non linear behavior for the total output energy and this non linearity arises due to the individual trend of the seeded SRS line describes in Figure 3.3 (a) for the third SRS line of hydrogen.

4 Conclusion

A comparative study of the relative intensities of the SRS lines of hydrogen and methane excited with 266 nm UV radiation was carried out. The SRS spectrum of methane showed only the SRS lines arise due to symmetric stretching mode of vibration of methane. The relative intensities of the SRS lines of methane showed quite a normal behavior, where as hydrogen exhibited a substantial intensity enhancement in third SRS line of hydrogen $(\breve{\nu}_3 = \breve{\nu}_0 - 3\nu_1)$ at 397.8 nm. The H-ε Balmer line (397 nm) generated due to dissociation and subsequent atomic emission gets seeded into the third SRS line and this seeding process brings about the enhancement of the signal. The excitation pulse energy dependence the conversion efficiencies of both methane and hydrogen were carried out.

References

[1] R. W. Minck, R. W. Terhune, and W. G. Rado, Laser stimulated Raman effect and resonant four photon interactions in gases H2, D2 and CH4, *Appl. Phys. Lett.* **3** (1963), 181–184.

[2] V. Krylov, A. Rabane, O. Ollikainen, D. Erni, U. Wild, V. Bespelov, and D.Staselko, Stimulated Raman scattering in hydrogen by frequency- doubled amplified femto Second Ti: sapphire laser pulses, *Opt. Lett.* **21** (1996), 381–83.

[3] V.G. Bespalov, D.I. Staselko, V. Krylov, A. Rebane, O. Ollikainen, and D. Erni, U. Wild, Structure of spectra of Stimulated Raman Scattering in high-pressure hydrogen, *Opt. Spectro.* **82** (1997), 384–389.

[4] F. Benapid, G. Antonopoulos, J. C. Knight. and P. J. Russell, Stokes amplification regimes in quasi-cw pumped hydrogen-filled hollow-core photonic crystal fiber, *Phys. Rev. Lett.* **95** (2005), 213903.

[5] Y. Uesugi, Y. Mizutani, S. G. Kruglik, A. G. Shvedko, V. A. Orlovich, and T. Kitgawa, Characterization of stimulated Raman scattering of hydrogen and methane gases as a

light source for picosecond time-resolved Raman Spectroscopy, *J. of Raman Spec.* **31** (2000), 339–348.

[6] I.G. Koprinkov, A. Suda, P. Wang, and K. Midorikawa, High-energy conversion efficiency of transient stimulated Raman scattering in methane pumped by the fundamental of a Femto second Ti:sapphire Laser, *Opt. Lett.* **24** (1999), 1308–1310.

[7] I. M. Tomov, P. Chen, and P. M. Rentzepis, Efficient Raman conversion of high-repetition-rate, 193 nm picosecond laser-pulses, *J. Appl. Phys.* **76** (1994), 1409–1412.

[8] D. A. Haner and I. S. McDermid, Stimulated Raman shifting of Nd: YAG fourth harmonic (266 nm) in H2, HD, D2, *IEEE J. Quantum Elec.* **26** (1990), 1292–1298.

[9] Roger Haydock and Ronald L. Te, Phys. Rev. B **57** (1997), 296.

[10] R. W. Hellwarth, Theory of Stimulated Raman Scattering, *Phys. Rev.* **130** (1963), 1850-1852.

[11] Chen-Show Wang, Theory of Stimulated Raman Scattering, *Phys. Rev.* **182** (1969), 482–494.

[12] R. S. McDowell and C. W. Patterson, Quasi-cw inverse Raman spectroscopy of the 1 fundamental of 13CH4, *J. Chem. Phys.* **72** (1980), 1071–1080.

[13] G. B. Jarvis, S. Mathew and J. E. Kenny, Evaluation of Nd:YAG pumped Raman shifter as a broad spectrum light source, *Appl. Opt.* **33** (1994), 4938–4946.

[14] D. W. Trainor, H. A. Hyman, and R. M. Heinricks, Stimulaed Raman scattering of XeF laser radiation in H2, *IEEE J. Quantum Electron.* **18**, 19821929–1934.

[15] M. A. Gondal, A. Dastageer, Z H. Yamani, and A. Arfaj, Investigation of stimulated Raman scattering of ν1 and ν2 fundamental and overtone modes Of CH4, *Chemical Physics Letters* **377** (2003), 249–254.

[16] J. M. Hollas, *High Resolution Spectroscopy*, John Willey and Sons, New York, 1998.

[17] G. V. Venkin, G. M. Mikheev, Stimulated Raman spectroscopy of excited states of the hydrogen molecule, *Sov. J. Quantum Electron* **15** (1985), 257–259.

[18] A. Sakoda, H. Mutoh, and K. Tsukiyama, Effect of externally injected radiation on amplified spontaneous emission in CO, *App. Phys. B* **72** (2001), 411–415.

[19] Z. Petrovic and V. Stojanovic, Anomalous doppler broadening of hydrogen lines due to excitation by fast neutrals in low pressure Townsend discharge, *Mem. S. A. It.* **7** (2005), 172–177.