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Stimulated Raman Spectroscopy for the Determination of Organic Compounds in Chemical Processes

by

Hassan S. Ghaziaskar, M.Sc.

A dissertation submitted to the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

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ABSTRACT

The theme of this research is to evaluate stimulated Raman scattering (SRS) as an analytical technique and to develop a SRS spectrometer for noninvasive, real-time monitoring of organic compounds in industrial process and effluent streams. The objective is to attain direct identification and determination of individual organic chemicals or compound classes without sampling, separations or other pretreatment procedures.

Firstly, the SRS activity of over one hundred organic compounds was measured at room temperature to explore the versatility of the SRS technique. SRS spectra were obtained successfully for all colourless neat liquids and their SRS shifts were studied systematically. It was confirmed that SRS Stokes shifts are usually the same as those found in spontaneous Raman scattering, with occasional differences in frequency from the strongest spontaneous Raman bands. Empirical trends have been observed in functional group recognition, compound classification, degenerate vibrational modes, substituent group effects, hydrogen bonding and concentration threshold. Other new observations such as multiple peaks, exceptional SRS activity and distributed spectra are also reported.

Secondly, several different ways of improving the detection limit and enhancing the analytical sensitivity of the SRS have been investigated. First, internally amplified SRS was developed as a novel approach to examine concentration thresholds in SRS. In the new physical model, it is proposed that amplifier molecules can be used to bridge the spatial gaps among analyte molecules distributed distantly from each other throughout a dilute solution. As a result, Stokes photons will effectively reach the next target

molecules down the pump light path to sustain and amplify the desirable SRS process. The model has been verified by experimental results which give a better understanding of the threshold phenomenon in SRS. The technique of internal amplification can practically eliminate concentration thresholds, leading to improved detection limits in analytical SRS measurements. Second, the effect of temperature on SRS was studied. Experimental results confirmed the theoretical prediction that higher gain and hence greater intensity can be obtained at lower temperature, as exemplified by the first-order Stokes line of ethanol or a 50%-by-volume solution of benzene in toluene. Third, experimental parameters such as cell length, cell position, focusing of laser beam, slit width, and signal integration time could be optimized. Experimental results also showed that the liquid flow rate had no effect on the SRS intensity. As a result, the detection limit and analytical sensitivity are not likely affected by changes in stream flow velocity. All in all, SRS has been developed as a useful analytical technique for the determination of medium to high levels of organic compounds in water and organic systems.

Thirdly, SRS was successfully applied to the screening of wines and liquors for low and high alcohol contents in their original bottles. Its ability in distinguishing between different inorganic acids was also established. Furthermore, it was demonstrated for the first time that SRS is a useful spectroscopic technique for the in-situ, non-invasive, and real-time monitoring of chemical processes such as polymerization reactions.

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PUBLICATIONS AND PRESENTATIONS

Five papers (published or accepted) and one manuscript (submitted) have been produced from this work:

- (1) H.S. Ghaziaskar and E.P.C. Lai, "Stimulated Raman Scattering in Analytical Spectroscopy", *Applied Spectroscopy Reviews*, 1992, 27(3), 245-288.
- (2) H.S. Ghaziaskar and E.P.C. Lai, "Temperature Effect on Stimulated Raman Scattering in Organic Liquids", *Canadian Journal of Applied Spectroscopy*, 1992, 37(4), 111-115.
- (3) L. Kutsera, H.S. Ghaziaskar and E.P.C. Lai, "Flow Injection Analysis for Beryllium Determination with Chrome Azurol S as Chromogenic Agent", *Analytical Letters*, 1992, 25(12), 2289-2304.
- (4) H.S. Ghaziaskar and E.P.C. Lai, "Internally Amplified Stimulated Raman Scattering", *Spectrochimica Acta*, 1993, 49A, 1003.
- (5) H.S. Ghaziaskar, W.M. Mullett and E.P.C. Lai, "Stimulated Raman Scattering Activity of Organic Compounds", *Vibrational Spectroscopy*, 1993, 5, 1.
- (6) E.P.C. Lai and H.S. Ghaziaskar, "Stimulated Raman Scattering for Alcohol and Acid Analysis", *Analytical Chemistry*, submitted, June 1993 .
- (7) E.P.C. Lai and H.S. Ghaziaskar, "Process Chemical Analysis of Polymerization by Stimulated Raman Spectroscopy", *Analytical Chemistry*, submitted, June 1993.

Two papers were presented:

- (1) H.S. Ghaziaskar and E.P.C. Lai, "Internally Amplified Stimulated Raman Scattering", #236, 38th Canadian Spectroscopy Conference, Peterborough,

Ontario, August 10-12, 1992.

- (2) H.S. Ghaziaskar and E.P.C. Lai, "Stimulated Raman Scattering for the Determination of Organic compounds in Process Streams", Varian Lectures, Carleton University, April 20, 1993.

Two posters were also presented at the Institute for Chemical Science and Technology conferences which were held in Toronto, 1990 and 1991.

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GLOSSARY

a_1	width factor of analyte (cm^{-1})
a_1'	width factor of amplifier (cm^{-1})
c	speed of light in vacuum (m s^{-1})
dB	decibel
E_T	stimulated Raman scattering (SRS) threshold energy (mJ)
f	focal length (cm)
g	total gain (cm W^{-1})
g_{exp}	experimental gain factor (cm W^{-1})
g_s	gain factor (cm W^{-1})
g_s'	gain factor of amplifier compound (cm W^{-1})
g_s''	modified gain factor [$= g_s (1-2\bar{n})$]
h	Plank's constant (J s)
$\hbar$	$h/2\pi$
I_p	pump-pulse peak intensity (W cm^{-2})
I_{pm}	Gaussian pump-pulse peak intensity (W cm^{-2})
I_s	SRS intensity (W cm^{-2})
I_{so}	spontaneous Raman scattering intensity (W cm^{-2})
$I_{s,\text{total}}$	integrated SRS intensity of analyte and amplifier (W cm^{-2})
k'	amplification coefficient
k_B	Boltzmann constant (J K^{-1})
N	number density (molecules cm^{-3})
n	refractive index of sample medium
$\bar{n}$	Bose factor $= [\exp(\hbar\omega_R/k_B T) - 1]^{-1}$
P_p	pump laser power (W)
P_R	power of Raman scattered line (W)
RSD	relative standard deviation
sr	steradian
T	temperature (K)
T_2	dephasing time (ns)
t_p	pump laser pulse width (ns)
v_e	thermal velocity of plasma electrons
z	pump laser path in sample (cm)
z_R	confocal length (cm)
$d\sigma/d\Omega$	spontaneous Raman scattering cross-section ($\text{cm}^2 \text{sr}^{-1}$)
$\Delta\nu_R$	SRS line width ($\text{radian}^{-1} \text{s}^{-1}$)
$\Delta\omega_R$	SRS line width (cm^{-1})
$\Delta\omega_{R,i}$	full width at half maximum (FWHM) of analyte or amplifier (cm^{-1})
λ_p	pump laser wavelength (nm)
λ_s	Stokes radiation wavelength (nm)
τ_B	acoustic phonon life-time (ns)
ν_p	pump laser frequency (s^{-1})
ν_R	Raman frequency of the vibration (s^{-1})
ω_0	radius of beam waist (cm)
ω_{as}	anti-Stokes frequency (cm^{-1})

ω_l	radius of unfocused laser beam (cm)
ω_{-m}	m th-order Stokes frequency = $\omega_p - m\omega_R$ (cm^{-1})
ω_p	pump laser frequency (cm^{-1})
ω_R	Raman vibrational frequency (cm^{-1})
$\omega_{R,\text{analyte}}$	analyte SRS shift (cm^{-1})
$\omega_{R,\text{amplifier}}$	amplifier SRS shift (cm^{-1})
ω_s	Stokes frequency (cm^{-1})
Ω	solid angle (sr)

CHAPTER I

INTRODUCTION

Stimulated Raman scattering (SRS) was first observed by Woodbury and Ng [1] using a nitrobenzene Kerr shutter as the Q-switch of a ruby laser, and then identified by Eckhardt et al [2]. If threshold requirements for the pump intensity and the interaction length were fulfilled for a given gain medium, SRS could be performed in a simple laser spectroscopy experiment [3]. A projected halo (or ring pattern) of blue-green light around the pump laser spot was observed on a card placed after a 5-cm-long cylindrical cell filled with toluene (Fig. 1). A measurement of the radius of the halo as a function of distance along the pump beam path would determine its origin to be a point inside the sample cell (Fig. 2) [4]. However, the halo would disappear if a 1-cm-long cell was substituted. Similar halos were observed for benzene over pump laser wavelengths, from 445 nm to 535 nm; the colors of the halos induced by different pump laser wavelengths would be slightly different.

If different liquids were inserted in the laser beam, different frequencies were emitted [5]. Each of them would be displaced from the laser frequency by an amount corresponding to a vibrational frequency of the liquids. Higher-order Stokes and anti-Stokes radiation rings could also be observed as the outer rings of the halo pattern [6,7].

Subsequent research unveiled the mechanism of the halo phenomenon [8]. The SRS radiation is the coherent nonlinear part of inelastic light scattering, which results from the interaction between light and molecular vibrations. The term nonlinear optics

Fig. 1. Graphical illustration of the SRS effect: (a) the apparatus and (b) the halos as rings of differing colors ($V_p \pm mV_R$) around the pump laser spot at the center.

Fig. 2.

Variation of the halo radius with distance along the pump laser beam.

refers to phenomena affecting the propagation of light which are dependent on other than the first power of the electric and magnetic field strengths [4]. Each spontaneous light scattering process has in principle a stimulated counterpart [9]. Under intense laser illumination, the simultaneous interaction of the molecules with two electromagnetic waves must be considered: the laser wave at frequency ω_p and the Stokes wave at frequency $\omega_s (= \omega_p - \omega_R)$. Both waves are coupled by the molecules vibrating with frequency ω_R . This parametric interaction leads to an energy exchange between the pump wave and Stokes (or anti-Stokes) waves [10] which may result in a strong directional output of the SRS waves as shown in Fig. 3 and many higher-order frequencies [11].

The angular distribution of intensity in SRS has been discussed in some of the first papers on the theory of the process [12-14]. Under suitable conditions, hydrogen produced a ring pattern in the transverse intensity profile of the conical SRS radiation [15]. Theoretical and experimental studies to understand the origin and behavior of the ring structure have been presented by Jin et al [16]. A set of equations for theoretical analysis and numerical simulations were derived. For a 25-cm-long cell containing hydrogen molecules at about 50 psi, Stokes light emerged on the surface of a cone with a nearly symmetric distribution around the forward axial direction. Over the range from 100 to 600 psi, the development of a central peak and a gradual decrease in the brightness of the ring (which eventually disappeared at the highest pressure values) were observed. It is apparent from the simulation results in Fig. 4 that the energy of the incoming laser beam was converted very efficiently into Stokes radiation, so that a pronounced minimum develops at the centre of the laser transverse profile. Further

Fig. 3. A schematic energy level diagram for SRS of a Raman-active molecule [11].

Fig. 4. Steady state (a) laser field intensity ($|F_L|^2$) profiles and (b) Stokes field intensity ($|F_S|^2$) profiles in different sections of the cell containing hydrogen gas at 300 K and 10 atm. $g = 3.638$ (corresponding to $g_s = 1.5 \times 10^{-9} \text{ cm W}^{-1}$; incident power density = 3 GW cm^{-2} ; cell length = 25 cm [16]).

along the longitudinal axis, the input beam broadened and weakened until, eventually, only a small central peak was left at the exit of the cell. The Stokes wave, instead, grew rapidly as it propagated through the cell and broadened until the ring pattern developed. The angle dependence of SRS can be derived from phase matching requirements and is graphically illustrated by Fig. 1, in which rings of color are shown for different orders of Stokes and anti-Stokes frequencies ($\omega_p \pm m\omega_R$) produced in the SRS process. Most of the converted frequencies are emitted within an angle of about 10° away from the laser beam direction.

The SRS technique shows two major advantages of strong signal levels [17] and resolution limited only by the laser linewidth in the gas phase [18]. Additionally, SRS is a self phase-matched interaction which is considerably less sensitive to minor beam depolarization and optical dispersion than other coherent Raman techniques [19]. The differences between the nonlinear stimulated and the linear spontaneous Raman effects are summarized as follow [10]:

- 1) While the intensity of spontaneous Raman lines is down by several orders of magnitude compared with the pump intensity, the stimulated Stokes radiations have intensities comparable to that of the pump wave.
- 2) The stimulated Raman effect is observed only above a threshold which depends on the gain of the Raman medium (i.e., molecular number density N , incident intensity I_p , spontaneous Raman scattering cross-section $d\sigma/d\Omega$) and the interaction length of the pump region in the scattering medium (z).
- 3) The SRS Stokes line will appear exactly at the band center of spontaneous Stokes scattering. Since amplification is more efficient close to the resonance

($\omega_s = \omega_p - \omega_R$), gain narrowing occurs. For narrow laser linewidths and under high gain conditions, the width of the stimulated Raman lines becomes notably smaller than that of the spontaneous lines [20].

- 4) For relatively long pump pulses of duration t_p greater than the vibrational dephasing time T_2 , the SRS excitation process is highly selective. Most Raman active substances show only one or two Stokes lines at frequencies $\omega_s = \omega_p - \omega_R$. Only the vibrational frequencies belonging to the sharpest and the most intense spontaneous Raman lines (i.e., with the largest scattering cross-sections or highest Raman gains g_s) show up. In the case of quasi steady-state, Raman lines with the highest gain value are stimulated first, but Raman modes with lower gain are also amplified (they only need a longer interaction length z). Under transient conditions ($t_p \leq T_2$) Raman lines with fast dephasing time T_2 gain importance. For $t_p \ll T_2$ the Raman line with the highest g_s/T_2 value is amplified preferentially [21]. In contrast, the spontaneous Raman scattering is independent of the pump laser duration [22].
- 5) Higher-order Stokes radiations (i.e., lines at frequencies $\omega_m = \omega_p - m\omega_R$) can be observed at exact harmonics of the first vibrational transitions for high gain systems [9]. This is easily understood as a multiple-step process; the intense first-order Stokes light serves as a pump source generating second-order Stokes radiation and so on.

Objectives of the Present Work

In the past, SRS has been used in variety of different applications such as production of widely-tunable radiation and efficient Raman shifting of laser wavelengths. A thorough list of SRS applications are given in Appendix I. However, the theme of this research, which represents an initiative to utilize SRS in the field of analytical chemistry, is to develop an SRS spectrometer for noninvasive, real-time monitoring of organic compounds in industrial process and effluent streams. The objective is to attain direct identification and simultaneous determination of individual organic chemicals or compound classes without sampling, separations or other pretreatment procedures. This work has been motivated by the great demand in industry for either quality control of their products or controlling potentially hazardous streams. Process analyzers are usually used to measure chemical components in an industrial process stream. Often it is only required to measure a key compound in the stream which is of concern for a specific reason.

CHAPTER II

THEORY

2.1 Exponential Gain

The starting condition for stimulated amplification is supplied by spontaneous Raman scattering. The SRS process continues to arise from the interaction of the molecules with not only the strong pump wave, but also the Stokes wave which can coherently stimulate Stokes scattering with intensities comparable to the pump wave [23]. SRS occurs when the gain equals the loss for the Raman transition with the lowest threshold. All further increases in pump power will go into the mode corresponding to the sharpest and most intense line in the spontaneous Raman spectrum, i.e., with the largest ratio of spontaneous Raman cross-section ($d\sigma/d\Omega$) to line width ($\Delta\omega_R = \Delta\nu_R/c$) [24]. In other words, the threshold argument for the observation of SRS predicts the existence of only one line in the stimulated spectrum for each molecule [23].

As nanosecond pulses have been used conventionally in SRS applications, the pump and Stokes pulses are much longer than the vibrational dephasing time T_2 . The theoretical treatments are hence based on steady-state Raman scattering. When an intense light pulse with peak intensity I_p traverses the sample medium, coherent excitation of molecular vibrations via SRS rises rapidly during the pumping process. The SRS intensity I_s grows exponentially along the pump path (z) of laser light through the interaction volume, and a positive gain at the Stokes frequency ω_s builds up an intense Stokes wave at the end of the sample.

$$I_s = I_{s0} \exp(g_s I_p z) \quad (1)$$

where g_s is the gain factor and I_{s0} is the seed intensity derived from spontaneous Raman scattering. The exponential build-up of Stokes power holds true until saturation occurs due to depletion of incident laser light and conversion of 1st-order Stokes radiation into higher-order ones [5].

SRS is isotropic in the plane perpendicular to the electric field vector of the incident light field. On the other hand, Stokes radiation in the forward or backward direction with respect to the incident laser beam finds a significantly larger interaction length than in transverse directions. As a result, Eq. 1 predicts that the exponential amplification of SRS parallel to the laser beam is drastically larger by several orders of magnitude [5].

Theoretically, the SRS gain factor (g_s) is related to the total differential spontaneous Raman cross-section per molecule ($d\sigma/d\Omega$, in $\text{cm}^2 \text{sr}^{-1}$) and the concentration (N = number density of molecules per cm^3) of the particular component giving rise to the non-linear optical effect according to [21,25-27]:

$$g_s = \frac{2c^2}{\pi \hbar n^2} \frac{N}{\Delta \nu_R (\nu_p - \nu_R)^3} \frac{d\sigma}{d\Omega} \quad (2)$$

where c is the speed of light in vacuum, $\hbar$ is Planck's constant, $\Delta \nu_R$ is the SRS line width, n is the refractive index of the sample medium, ν_p is the pump laser frequency, and ν_R is the frequency of the Raman-active molecular vibration. Eq. 2 predicts a frequency dependence of g_s which follows the shape of the spontaneous Raman band. Any attempt to increase the Raman cross-section and to reduce the line width will increase the gain. For instance, a decrease in temperature may increase $d\sigma/d\Omega$ and

reduce $\Delta\nu_R$ which will lead to a higher I_s as reported recently [28]. The Raman cross-section $d\sigma/d\Omega$ is related to experimentally measurable quantities by the equation $d\sigma/d\Omega = P_R/P_p N z \Omega$ where P_R is the Raman power for the whole line scattered into the solid angle Ω and P_p is the pump laser power. Subsequent to coherent excitation, the molecular vibration decays during a free relaxation with the characteristic time constant T_2 [29]. The dephasing time T_2 of a Raman scattering medium is proportional to the inverse of the scattering line width ($T_2 = 1/\pi\Delta\nu_R = 1/\pi c\Delta\omega_R$) [30] and are on the order of several picoseconds for polyatomic molecules at room temperature [29]. Eq. 2 may now be written as:

$$g_s = 2(\lambda_s^3 N T_2 / c h n^2) (d\sigma/d\Omega) \quad (3)$$

where λ_s is the wavelength of Stokes radiation.

2.2 Threshold

The threshold of SRS has usually been defined as the point where 1% of the pump intensity has been converted to the Stokes intensity [31-32], i.e., $I_s/I_p = 10^{-2}$. The threshold for SRS depends on I_p when the pulses are much longer than T_2 , and on the pump fluence (i.e., flux per unit area, $J\ cm^{-2}$) when the pulses are much shorter than T_2 . For polyatomic molecules in the liquid state at 300 K, T_2 is very short and frequently of the order of picoseconds [33]. Assuming a gaussian pump pulse shape with I_{pm} as the peak intensity, we get the expression

$$g_s I_{pm} z = 25 + 131.5 T_2 / t_p \quad (4)$$

Recognizing that the Stokes beam grows from spontaneous Raman scattering, the gain required to reach the threshold is about $\exp(25) = 7.2 \times 10^{10}$ [5,27,31]. However,

focused pump beams are normally used in SRS. Assuming a gaussian beam profile, we get an expression for the threshold energy for SRS (E_T) as a function of pulse width [34]

$$E_T = (4.2t_p + 22.3T_2)\lambda_p/g_s \quad (5)$$

where λ_p is the pump wavelength.

For a strong Raman line, $d\sigma/d\Omega \cong 5 \times 10^{-30} \text{ cm}^2\text{sr}^{-1}$. For $N \cong 10^{22} \text{ cm}^{-3}$ in liquids and $T_2 \cong 10^{-12} \text{ s}$, Laubereau estimated the gain factor to be $g_s \cong 10^{-9} \text{ cm W}^{-1}$ from Eq. (3). A value of $2.5 \times 10^{10} \text{ W cm}^{-1}$ for the product, $I_p z$, is necessary for amplification of the Stokes wave by a factor of $\exp(25)$ [5]. This corresponds to 2.5 GW cm^{-2} over a cell length of 10 cm. This value is in good agreement with the experimental threshold intensity of $\sim 5 \text{ GW cm}^{-2}$ determined for benzene. Small-scale self focusing was found to be essential for the low threshold of efficient SRS and the simultaneous stimulation of two vibrational modes [21].

The interaction length of the pump beam and the SRS-active sample may be increased in order to attain the threshold condition more easily. It was shown that a longer path length lowered the threshold pump power required for neat benzene when a 250-cm-long hollow core fibre was used [35]. It was demonstrated that there was a factor of 30 improvement in the required threshold power for a 250-cm-long hollow-core fibre in comparison with a 5-cm-long cylindrical cell. The possibility of studying SRS-active organic compounds in hollow-core optical fibers to provide extended sensitivities should be interesting [19]. Gorner et al measured the frequency dependence of the gain factors of SRS in CCl_4 and C_2Cl_4 , when the liquids were contained in a hollow glass fibre (10 μm diameter) to obtain high intensity over a 1-km interaction length. Peak gain factors of 1.3×10^{-9} and $1.7 \times 10^{-9} \text{ cm W}^{-1}$ were obtained at 458 and 447 cm^{-1} , respectively

[36]. High-intensity SRS radiation was also obtained by Zolin et al in a quartz capillary filled with benzene or with a mixture of benzene and other aromatic compounds [37].

For D_2 contained in a 40-cm-long capillary, the threshold laser power decreased by a factor of 4 when the pressure of D_2 was increased from 15 to 40 atmospheres [32]. Also, the threshold could be lowered by micron-size droplets for nonlinear optical processes, by several orders of magnitude. This lowering of the threshold is obvious in the sense that while the laser power may be low, the electromagnetic field is locally enhanced through the redistribution of energy by the droplet [38], to reach again the threshold intensity for the SRS effect [39].

Multipass cells of different designs had been used to enhance the SRS efficiency in materials which had no significant optical absorption (at the pump laser wavelength). In a multipass geometry, the laser beam was used repeatedly by reflecting it back and forth through the cell. Two previous designs involved either ellipsoidal light traps [40] or top mirrors [41]. For ellipsoidal light traps, calculations showed that gains on the order of 500 should be attainable with low-eccentricity ellipsoids. An experimental gain of 93 over the single-pass case was obtained when SRS radiation from atmospheric N_2 was measured with a 0.2-eccentricity ellipsoid. The top-mirror approach has been, however, more commonly employed because of its simplicity. With high-reflectivity (i.e., low-loss) mirrors, net gains of 20 - 30 were realized using cw gas lasers and a focal volume of 1.1 mm x 0.3 mm x 0.3 mm. Other multipass cells were devised for pulsed Nd-YAG lasers, giving resultant gains as high as 42 [42]. In practice, all of the multipass schemes required high-quality, near-diffraction-limited laser behaviour and good optical quality in the medium (i.e., modest and stable refractive index gradients,

low turbulence levels, etc.) [43].

2.3 Internally Amplified SRS

Internally amplified SRS (IASRS) is a novel approach to studying the phenomenon of concentration threshold. It gives a better understanding of the physical picture of SRS and is useful for lowering the threshold in analytical SRS measurements.

The presence of a concentration threshold in the SRS process may be visualized by a large distance between separate molecules in a dilute solution. Consequently the possibility of one molecule being struck by Stokes photons generated from neighbouring molecules becomes negligible. This model implies that if additional Stokes photons are provided by an amplifier (i.e., Stokes-photon generating) compound for optical stimulation of the analyte, SRS will become feasible even in dilute solutions. When these two SRS-active compounds are present in the same solution and have similar Raman shifts ($\omega_R = \omega_p - \omega_s$), Eq. 1 may be rewritten as:

$$I_{s,\text{total}} = I_{s0} \exp\{(g_s + k'g_s')I_p z\} \quad (6)$$

where g_s and g_s' are the gain factors of the analyte and amplifier compounds, respectively. The amplification coefficient, k' , is proportional to the degree of overlap of the two SRS Stokes bands. As the difference in SRS shifts of analyte and amplifier increases, the degree of amplification will be reduced. In other words, the more the analyte and amplifier Stokes shifts overlap, the more amplification can be expected.

The amplifier compound can be added to the analyte solution to augment the gain above the SRS threshold. This will produce a measurable $I_{s,\text{total}}$ which makes the determination of trace analytes possible. Since SRS shifts in liquid media usually have

fairly broad bandwidth (10-60 cm⁻¹), the choice of an appropriate amplifier compound is straight forward to match the SRS shift of the analyte in order to maximize the amplification coefficient. Two comprehensive lists of newly observed and formerly reported SRS-active compounds are given in the next chapter and Appendix II [44], respectively.

Theoretical analysis and numerical simulation of amplification coefficients for different analyte and amplifier SRS shift separations and line widths will be performed in this work. Vibrational transitions in liquids are inhomogeneously broadened and the interaction of a molecule with surroundings frequently leads to slight changes of the SRS frequencies. Therefore, the Raman lines no longer have a Lorentzian shape [33]. Gaussian analyte and amplifier SRS intensity profiles are represented by these equations:

$$I_s \exp \left[-0.5 \left(\frac{\omega_R - \omega_{R, \text{analyte}}}{a_1} \right)^2 \right] \quad \text{and} \quad I'_s \exp \left[-0.5 \left(\frac{\omega_R - \omega_{R, \text{amplifier}}}{a'_1} \right)^2 \right] \quad (7)$$

where I_s and I'_s are the amplitudes of the analyte and amplifier SRS intensity profiles, $\omega_{R, \text{analyte}}$ and $\omega_{R, \text{amplifier}}$ are the analyte and amplifier SRS shifts (in frequency units). a_1 and a'_1 are the width factors of the analyte and amplifier SRS intensity profiles which are related to the full width at half maximum ($\text{FWHM} = \Delta\omega_{R,i}$):

$$\Delta\omega_{R, \text{analyte}} = 2\sqrt{2\text{Ln}2}a_1 \quad \text{and} \quad \Delta\omega_{R, \text{amplifier}} = 2\sqrt{2\text{Ln}2}a'_1 \quad (8)$$

The k' parameter may be calculated by multiplying the two Gaussian profiles and integrating the product:

$$\begin{aligned}
 k' &= \int_{-\infty}^{\infty} \exp \left[-0.5 \left(\frac{\omega_R - \omega_{R, \text{analyte}}}{a_1} \right)^2 \right] \exp \left[-0.5 \left(\frac{\omega_R - \omega_{R, \text{amplifier}}}{a_1'} \right)^2 \right] d\omega_R \\
 &= \exp \left[-\gamma - \alpha \left(\frac{\beta}{2\alpha} \right)^2 \right] \int \exp \left[\alpha \left(\omega_R + \frac{\beta}{2\alpha} \right)^2 \right] d\omega_R \quad (9)
 \end{aligned}$$

where

$$\alpha = -0.5 \left(\frac{1}{a_1^2} + \frac{1}{a_1'^2} \right), \quad \beta = \frac{\omega_{R, \text{analyte}}}{a_1} + \frac{\omega_{R, \text{amplifier}}}{a_1'}, \quad \text{and} \quad \gamma = 0.5 \left(\frac{\omega_{R, \text{analyte}}^2}{a_1^2} + \frac{\omega_{R, \text{amplifier}}^2}{a_1'^2} \right)$$

It may be proved that

$$\int_{-\infty}^{\infty} \exp \left[\alpha \left(\omega_R + \frac{\beta}{2\alpha} \right)^2 \right] d\omega_R = \sqrt{\frac{\pi}{-\alpha}} \quad (10)$$

Hence, k' becomes:

$$k' = \sqrt{\frac{\pi}{-\alpha}} \exp \left[-\gamma - \frac{\beta^2}{4\alpha} \right] \quad (11)$$

Thus, k' may be calculated for various $\omega_{R, \text{analyte}}$ and $\omega_{R, \text{amplifier}}$ separations as reported in next chapter.

2.4 Temperature Effect on Stokes Intensity in SRS

Studies related to the effect of temperature on SRS intensity were started by Minck et al who plotted the calculated and experimental Stokes gain factors, g_s and g_{exp} , for both D_2 and H_2 as a function of temperature based on the population and width of various vibrational-rotational states [45]. They showed that competition between various simultaneously stimulated SRS transitions could be observed by varying the temperature of the gas. The level crossover from $Q_1(2)$ to $Q_1(1)$ and shift from $Q_1(1)$ to $Q_1(0)$ were vibrational Raman-vibrational Raman competition. In the lower temperature range only SRS from one of the vibrational levels, $Q_1(0)$, was observed while the $Q_1(1)$ and $Q_1(2)$ transitions were strongly suppressed. The second type of competition, between vibrational and rotational Raman transitions, was not as strong as that between two vibrational Raman transitions. Only at very low temperatures where $S_0(0)$ was very strong were the $Q_1(J)$ transitions finally suppressed [46]. In D_2 this was caused by a variation in population of the different rotational levels of the gas molecule [47]. The competition between different vibrational Raman transitions at various sample temperatures may lead to the observation of different orders of SRS lines or change of Raman shifts. This characteristic may be utilized in qualitative and quantitative works to differentiate between the chemicals with close or overlapped Raman shifts.

Johnston et al calculated the steady-state gain factor for several crystalline materials [48]. In these gain calculations for small frequency shifts, they included the Bose factor $\bar{n}$ which was a thermal population factor of the vibrational mode:

$$g_s'' = g_s (1 - 2\bar{n}) \quad (12)$$

$$\text{with} \quad \bar{n} = [\exp(-\omega_R/k_B T) - 1]^{-1} \quad (13)$$

where k_B is Boltzmann's constant, T is the liquid temperature, and $\hbar = h/2\pi$. In general, higher gain was obtained at a sample temperature of 80 K in comparison with 300 K, and different extent of gain enhancement were observed for different crystals. For example, the SRS gain of LiNbO_3 and LiTaO_3 decreased rapidly to an impractical level with increasing temperature in the range of 375-475 K. They also reported that cooling $\text{Ba}_2\text{NaNb}_5\text{O}_{15}$ to liquid nitrogen temperature reduced the line width by nearly a factor of three, with a corresponding increase in SRS gain. In addition, Raman shifts (ω_R) increased when the samples were cooled down to 80 K. This temperature variation characteristic (going from 300 to 80 K) was used to precisely tune the frequency in a Raman oscillator over a substantial radio-frequency range (e.g., 300 GHz for LiNbO_3).

Since the Bose factor decreases with decreasing temperature according to Eq. 13, any attempt to reduce the sample temperature would increase the modified gain factor (g_s'') and consequently the SRS intensity assuming that the other parameters in Eqs. 13 and 2 do not vary significantly with temperature over a small range and may be regarded constant for a given molecule.

2.5 Interferences

Firstly, there is a strong dominance effect when more than one Raman active material is present. Stimulated Raman emission at the weaker lines is inhibited by the emission at the stronger line. This is probably a consequence of the depletion of primary laser radiation by Raman conversion at the stronger line. For example, nitrobenzene was strongly Raman active and tended to suppress the SRS action in cyclohexane and substituted aromatic compounds except benzene. With benzene in the cavity, however,

the nitrobenzene lines were quenched and appeared only at very high excitation energy and then only weakly [49].

Secondly, as a consequence of the large values of pump laser intensity required to reach the SRS threshold, other competing nonlinear effects may occur in many SRS experiments [5]. There are two nonlinear processes which appear frequently together with the SRS: the optical self-focusing [9] and self-trapping [50] of the incident laser beam, and the generation of stimulated Brillouin scattering (SBS) [51]. Quantitative investigations showed that the steady-state SBS gain factors of liquids are frequently one order of magnitude larger than the gain factors for SRS [36,52,53]. Therefore, the SBS competes successfully with SRS in many substances. In fact, SRS is suppressed or even extinguished when most of the laser light is quantitatively converted into Brillouin light [53]. For a quantitative study of the SRS effect, the experimental conditions have to be carefully adjusted to avoid disturbing other nonlinearities. For instance, the generation of SBS is greatly reduced at excitation times smaller than the phonon life time [54], and SRS can freely develop [55]. With sufficiently short (ns) pulse durations, the gain factor for SBS can be reduced drastically [56]. Alternatively, the use of a laser light source with a band width exceeding the Brillouin line width (of the order of several hundred MHz) will suppress SBS effectively [36].

Thirdly, the SRS emission may be suppressed by sample absorption. This might be considered as a disadvantage for SRS measurement of water and aqueous solutions if the pump laser and/or Stokes frequencies are in the infrared region [57].

CHAPTER III

EXPERIMENTAL

A variety of experimental setups with different lasers and other components have been tested for their usefulness in SRS measurements. Their designs were based on the successful setups already reported in the literature [4,58-63].

The schematic diagram of the first experimental setup (setup 1) used in this work is shown in Fig. 5. A Photon Technology International (London, Ontario) PL-202 dye laser was pumped by a PL-2300 N₂ laser. The laser pulses, having 500-nm wavelength (λ_p) and 500-ps pulse width (t_p), were spatially filtered by an aperture and focused by a 10-cm-focal-length lens into a cylindrical sample cell (2-10 cm long). A relatively small laser spot size at the waist was chosen on the basis of the idea of producing as much SRS radiation as possible with a low laser pulse energy to keep the laser energy density below the damage thresholds of the sample and optical components. The SRS lines, were resolved from the laser frequency by a Jarrell-Ash 82-518 0.5-m Ebert spectrograph (or monochromator) with a 1180-lines/mm grating and detected by a photomultiplier tube (PMT). A stepping motor and controller was installed on the monochromator to convert it to a scanning spectrometer. This permitted automation of the SRS spectral measurement, saving substantial operator efforts involved in manual scans. However, a single spectrum still required a total acquisition time on the order of 40 min.

Later, a Princeton Instruments (Trenton, New Jersey) RY-1024 photodiode array

Fig. 5. Experimental setup 1 for SRS spectral measurements. PDA = photodiode array.

(PDA) detector was used for simultaneous multiwavelength measurement of SRS intensities to realize real-time monitoring of the changing concentrations of more than one compound in a flow stream. The PDA offers many advantages such as wide spectral response (180 - 1060 nm), a small pitch width (25- μ m cell-to-cell spacing), and a large aperture (2.5 mm) to ensure that the entire laser beam will be sampled thus preventing errors due to the natural intensity variations across the diameter of the pump laser beam. The system has a low dark current of 8 counts s^{-1} diode $^{-1}$, a signal-to-noise ratio (S/N) performance of 10000:1, and a large dynamic range of 1:16000. Most importantly, the sampling time required to scan all 1024 elements is only 10 ms, hence minimizing the analysis time and enabling the system to be used for tracking the changing concentrations of analytes in a flow stream. Use of the PDA allowed an entire 1283- cm^{-1} window of the SRS spectrum to be simultaneously acquired, with an effective spectral resolution of 2.5 cm^{-1} . Data acquisition and array timing were supervised by an ST1000, OSMA software developed by Princeton Instruments. Each spectrum was acquired over a pre-selected exposure time while avoiding saturation of the photodiodes, and spectra were accumulated in order to improve the S/N. Background subtraction might be implemented subsequently to remove both the continuum and any non-analyte lines. Essentially, the system includes a complete software package required to reduce the enormous amount of data acquired by the detector to a manageable level in real time.

A more powerful laser was incorporated in the second experimental setup (setup 2) for SRS spectral measurements, as shown in Fig. 6. A Lumonics (Rugby, Warwickshire, England) HY400 Nd-HyperYAG pulsed laser was used to optically pump the sample. The frequency-doubled laser pulses ($\lambda_p = 532$ nm, $t_p = 10$ ns), operated

Fig. 6. Experimental setup 2 for SRS spectral measurements. LLF = laser-line absorption glass filters; HNF = holographic notch filter.

at a repetition rate of 5 Hz, were focused by a 20-cm-focal-length lens into a 50-cm-long cylindrical sample cell. The outgoing radiation was passed through a couple of laser-line absorption glass filters (LLF) and a holographic notch filter, HNF, (Kaiser Optical Systems, Ann Arbor, Michigan) in order to isolate the Stokes-shifted SRS lines from the residual pump laser light. A planoconvex lens focused the SRS lines which were directed by two prisms onto the entrance slit of the Jarrell-Ash 82-518 Ebert monochromator. Instead of one of the right-angle prisms, an equilateral prism could be used to disperse the laser and SRS lines. This configuration was useful in lowering the background signal due to SRS activity of the solvent and residual laser light in quantitative SRS works. The SRS spectrum was monitored by the PDA detection system. The spectral window was scanned from 400 nm to 700 nm at regular intervals in order to monitor the entire SRS spectrum for each of the compounds examined (see Table 1). All spectra were obtained at room temperature using reagent-, analytical- or spectro-grade chemicals as dictated by availability. The presence of low amounts of impurities would not affect the SRS spectrum owing to the dominance effect of the major components.

For intensity measurements of a single SRS line the instrumentation could be simplified by using a PMT and interference band-pass filters as shown in Fig. 7 (setup 3). The SRS line, after passing through a HNF and an interference band-pass filter, was detected by a PMT which was not cooled and applied with a low voltage of 350 V to reduce the dark current and the background signal mentioned above. The large size of the PMT entrance port helped alleviate signal fluctuations due to laser pointing errors. The pulsed PMT output signal was processed by a gated integrator and boxcar averager over 300 pulses. A digital multimeter monitored the amplitude of the averaged signal.

Fig. 7. Experimental setup 3 for SRS intensity measurements. PMT = photomultiplier tube.

Back-scattered SRS intensity was measured as shown in Fig. 8 (setup 4). The Nd-YAG laser beam is deflected by a right angle prism onto a holographic beamsplitter, HBS, (Kaiser Optical Systems). HBS directs the laser beam onto the sample cell and lets the back-scattered SRS light pass through it. The back-scattered Stokes line after being resolved from solvent and residual laser lines by a pair of HNFs and two band-pass interference filters is detected using a PMT. Data acquisition instrumentation was similar to what was used in setup 3 as shown in Fig. 7.

One of the major causes of imprecision in SRS measurements, and hence a relatively poor detection limit and ill-defined threshold value, is fluctuations in the Stokes intensity. When a photodiode array served as the detection system (see Fig. 6), the relative standard deviation (RSD) for 15 replicate SRS measurements was found to be 0.46% typically. After much experimental investigation, laser pointing errors and fluctuations in conical SRS generation at the entrance slit of the monochromator were significantly alleviated by using a PMT equipped with interference band-pass filters as the detector (see Fig. 7). These fluctuations arise as a result of uncertainty in the time, the position within the sample cell, and the direction within which the first few spontaneous Raman photons are emitted [64]. The probability that the conical Stokes beam (centroid) will propagate in a given direction has been calculated theoretically by Walmsley. It was shown that the angular stability of the centroid is $\sim 10\%$ of the pump beam divergence angle for a uniformly pumped, cylindrical Raman cell.

Experimental setup 2 was used in IASRS investigations. The resolution of the system would not affect the internal amplification as long as the spectral bandpass of the optical detection system was sufficiently large to accommodate both the analyte and

Fig. 8 Experimental setup 4 for back-scattered SRS intensity measurements. HBS = holographic beamsplitter.

amplifier SRS peaks for total intensity measurements. Each spectrum is an in-memory accumulation of 125 spectra, each acquired over an integration time of 0.02 seconds (corresponding to 2 scans), in order to improve the S/N while avoiding saturation of the photodiode array. Peak areas of the peak SRS line for different concentrations were used to construct a standard calibration curve.

The effect of temperature on SRS Stokes intensity was investigated using experimental setups 1 and 2 with a jacketed cell (see Fig. 5) for temperature control. Pulsed laser excitation was used to advantage in minimizing the amount of heat deposited in the sample; the duty cycle of each pulse was so small that it produced negligible heating. Initially a mixture of liquid nitrogen and different organic solvents was used in the cell jacket to cool down the sample in the inner cell from 21 to 10 °C [65]. In order to incorporate a wider range of temperature a flow of ethanol coming from a HAAKE (Dieselstraße, Federal Republic of Germany) Cryostat F3-Q heating bath and circulator was used in the cell jacket to control the temperature of the sample in the inner cell anywhere from -60 to 50 °C. Nitrogen gas was continually blown over the cell windows to prevent moisture condensation. Since freezing of water and other impurities in the sample made a cloudy solution, no SRS signal was measured below -20 °C in this study.

The HAAKE cryostat F3-Q heating bath and circulator was used next again at room temperature to introduce ethanol to the sample cell for investigating the effect of flow velocity on SRS Stokes intensity. A liquid flow meter was placed in line at the outlet of the circulator to measure the changing flow rate (from 0 to 30 l min⁻¹) before the intensity of the Stokes line of ethanol at 2928 cm⁻¹ was measured.

A multipass cell was designed, as shown in Fig. 9, to enhance the SRS efficiency

Fig. 9. A multipass cell for SRS measurements.

so as to lower the detection limit or the threshold laser power. The concave face of the meniscus lens was coated with aluminum oxide except for a circular aperture in the centre. The pump laser beam was passed through the aperture and focused into the sample cell. Upon exit from the cell, the beam was reflected back into the cell by a right-angled prism (which was positioned slightly off the beam axis). As a result, the pump laser beam traversed the sample several times before the optically induced SRS radiation was collected by a 0.5" right-angled prism. The surfaces of the lenses and prisms were covered with a proper antireflection coating to eliminate reflection losses. Note that ultimately wave guiding in liquid-filled optical fibres or capillaries will be the most effective way to increase the interaction length.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 SRS Activity of Organic Compounds

A wide range of functional groups that exhibit strong SRS activity are of interest to organic analytical chemists for the identification and determination of molecules. SRS can be observed in different solid, liquid and gaseous materials. For instance, SRS activity was measured in anthracene crystals with $\sim 1\text{-}\mu\text{m}$ thickness using a nitrogen laser (pumping wavelength = $\lambda_p = 337\text{ nm}$, peak power = 3 kW , pulse width = $t_p = 12\text{ ns}$) [66]. The SRS of water and aqueous solutions were studied by several groups to investigate microscopic water structures [57]. With a KrF laser system ($\lambda_p = 248\text{ nm}$, $t_p = 20\text{ ps}$, pulse energy $\leq 200\text{ }\mu\text{J}$) SRS was observed in hydrogen, ammonia, methane and sulfur hexafluoride below 5-atm pressure. Under the same conditions, however, no SRS could be obtained in oxygen or nitrogen [34]. Currently, the SRS of complexes and clusters in supersonic molecular beams is being investigated by Felker [67].

In this section we report the newly observed SRS activity of over one hundred organic compounds in order to demonstrate the capability of SRS for analysis of organic compounds. The results are summarized in Table 1. They are estimated to be accurate within $\pm 3\text{ cm}^{-1}$. Some of the compounds exhibited more than one Stokes shift, making the interpretation of these spectra very challenging. A comprehensive list of formerly reported SRS active compounds including their SRS shifts and gain factors, is also given

in Table 5, Appendix II. These compounds are mostly colourless alcohols, esters, halogenated chemicals, substituted hydrocarbons and benzene derivatives. They are listed in increasing order of Stokes shifts. Unlike the prediction of Kaiser et al, [23] more than one SRS line was observed for many compounds and these lines are arranged in decreasing order of intensity within each compound. Our systematic studies confirmed that SRS peaks appear at the same Stokes shifts as those observed in spontaneous Raman scattering. For compounds which have more than one Stokes order, higher-order Stokes shifts are given as an integral multiple of the 1st-order Stokes shift. In cases where a sharp and well-defined single SRS peak was not observed, the base width of the broadened group of peaks is specified in parentheses.

Table 1. Newly observed SRS activity of organic compounds.

Compound	SRS Stokes Shift (cm ⁻¹) ^a
Hexafluorobenzene	562, 589 2 x 562 3 x 562 4 x 562 5 x 562 6 x 562
Dihydropyran	837 2927 1671
Polystyrene	994
Benzylamine	1000 2 x 1000 3054
α -Methylstyrene	1001 1630 3070 (3047-3094)
Phenyl-2-propanone	1001 2 x 1001 3 x 1001 3057
Styrene oxide	1001 2 x 1001 3065 4062
Cumene	1001 (991-1010) 2 x 1001 3067 (3047-3094)
Iodobenzene	1001

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
Benzyl acetate	1004 2 x 1004 3068 (2906-3130) 4 x 1004 (3998-4111)
Formamide	1387 2740-3120
1,1,2-Trichloroethylene	1538 609
Hexachloro-1,3-butadiene	1603 415
Isosafrole (C ₁₀ H ₁₀ O ₂)	1657
Acrylonitrile	2225 (2190-2332) 2 x 2225 (4364-4545) 1610
Methacrylonitrile	2229 2 x 2229 5094-5232
Dimethyl sulfoxide	2772
Methylal (Dimethoxymethane)	2827 2842 2812 2855
Trimethylamine	2833
Malonaldehyde tetramethyl acetal	2837 2949 2722 3061 3169 2612 3286

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
	2493
	3381
Isopropyl cyclohexane	2845
	2929
Undecane	2851
2-Undecanone	2851
	2916
	2984
	2784
Undecyl alcohol	2851
Nonyl alcohol	2852
	2869
Methyl myristate	2853
2-Methylcyclohexanol	2860
	2936
	3011
	2776
Ethanolamine	2861
Amyl alcohol	2864
1-Heptene	2866
1,3,5-Triisopropylbenzene	2867
	1001
Bis(2-ethylhexyl) phthalate	2868
	2918-2966
3-Methylcyclohexanone	2869

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
n-Butyl bromide	2871 2934 2997 2810
n-Butyl ether	2871
2,2-Oxydiethanol	2872
1-Bromo-3-methyl butane	2872
Di-2-heptanol	2873
2-Ethyl 1-hexanol	2873
Tri-n-butyl phosphate	2906 2942 2838
Bis[2-(2 methyloxy ethoxy)] ethyl ether	2874 2326
2-Octanol	2874 2930
Hexanoic acid	2875 2936 2918
n-Butyl chloride	2877 2943 2816 3003
3-Pentanol	2877 2938 2995 2821

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
3-Methylpentane	2878 2858 2934 2896
n-Butyl nitrate	2879 2940
Glycerol	2883 2894
3-Octanone	2890 2869 2930
3-Methoxy-1,2-propanediol	2896 2939 2837
2,2,4-Trimethylpentane	2896 2x2896
1-Octene	2905 2934
3,5,5-Trimethyl-1-hexanol	2906
Iso-octane	2908 2873 2944
1-Chloro-3,3-dimethylbutane	2910
2-Methyl-2,4-pentanediol	2910 2933
Dibutyl phthalate	2912 (2669-3099)
Trans,trans,cis-1,5,9,-cyclodecatriene	2912

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
2,4-Dimethyl-3-pentanone	2915 2874 2953
Formaldehyde	2916 (2717.2-3174.4)
Cyclooctene	2917 2857
Tri-isopropyl borate	2919
2-Pentanone	2920
p-Cymene (p-Isopropyltoluene)	2924 (2827-3071) 802 (780-844) 1211
4-Chloro-o-xylene	2928 (2897-2998) 740
n-Methylacetamide	2929
2-Chloro-2-methylpropane	2930
2-Methyltetrahydrofuran	2930 2998 2867
1-Hexene	2931
Methyl methacrylate	2931
Ethyl octanoate	2931 2873
3-Heptanone	2934 2871 2896
Triethyl orthoformate	2935

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
Triethyl phosphate	2935
4-Bromo-o-xylene	2935 (2692-3173)
Ethyl chloroacetate	2937 2962
Ethyl iso-valerate	2937 2873
Hexyl acetate	2937
Triethyl benzene	2938
Methyl acetate	2939
Iso-amyl acetate	2940 2874
Methyl butynol	2941 2112
Ethyl formate	2942
Ethyl oxalate	2942
Ethyl phthalate	2942 (2722.4-3127.9)
Ethyl propionate	2942
Propionaldehyde	2943 2890
Acetonitrile	2944
Diethyl phthalate	2948
3-Hydroxytetrahydrofuran	2949
Propionic Acid	2950

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
Formic Acid	2952 (2722-3128)
2,5-Dimethyloxytetrahydrofuran	2954 2833
Pentamethylene chlorohydrin	2954
Glutaric dialdehyde	2955
Methyl formate	2961
Dimethyl carbonate	2962
Fluoroacetic acid	2963
1-Bromo 3-chloro pentane	2968 (2935-2983)
Nadic methyl anhydride	2988
Allyl alcohol	3013 1642
Hexachloro-1,3-butadiene	3208
Methylamine	3317
Benzoic acid (saturated in water or ethyl ether)	NA ^b
o-Chloroaniline ^c	NA
18-Crown-6 ether (saturated in benzaldehyde)	NA
30-Crown-10 ether (saturated in THF)	NA
4 (2,4-Dichlorophenoxy) butyric acid (saturated in ethanol)	NA

(continued)

Table 1 (continued)

Compound	SRS Stokes Shift (cm ⁻¹)
Glycine (saturated in water)	NA
L-proline (81% in water)	NA
Phenol	NA

^a full width at half maximum of SRS peak is $\sim 10\text{-}20\text{ cm}^{-1}$ for our setup.

^b NA = not SRS active under the present experimental conditions.

^c slightly yellowish in colour.

From the empirical trends for the newly observed compounds (see Table 1) and previously reported ones (see Appendix II) studied by the SRS technique, the following general statements may be made:

- 1) Every colourless neat organic liquid, whether it be a chain or a ring in molecular structure, exhibits SRS activity as a universal property. Coloured liquids (e.g., o-chloroaniline), however, absorb the excitation laser light and attenuate the Stokes wave intensity to prevent stimulation. Furthermore, SRS only occurs when the gain equals or exceeds the loss for the Raman transition with the lowest threshold.
- 2) The SRS spectrum consists of regions that are useful for functional group recognition. For example, the C=C stretching vibration for olefins exhibits very strong scattering, resulting in an intense SRS peak which, like the spontaneous Raman scattering band, occurs at $\sim 1600\text{ cm}^{-1}$.
- 3) Since SRS originates from specific Raman-active vibrational mode (e.g. C-H

stretching, ring breathing, etc.), the SRS shifts of a similar class of compounds are centred about a certain spectral region. For instance, the SRS peaks of alcohols are all located at $2925 \pm 88 \text{ cm}^{-1}$ and all of the SRS peaks of benzene derivatives fall within the range from 944 to 1034 cm^{-1} . However, some of these compounds exhibit additional Stokes shifts in other regions of the SRS spectrum.

- 4) SRS is a diagnostic tool which is useful for screening purposes to differentiate various groups of compounds (viz., alcohols, esters, benzene derivatives, and halogenated chemicals). For instance, among those compounds which contain a benzene ring, the ring breathing mode dominates in the spectra of benzenes and naphthalenes, the C=C stretching vibration is dominant in the spectra of ethylenes and butadienes, whereas the C-H stretch is the most intense band in the spectra of propanes and higher homologues.
- 5) The Stokes shifts belonging to the sharpest and the most intense spontaneous Raman lines usually show up in the SRS spectrum, in accordance with the macroscopic theory of SRS. Occasional differences in frequency from the strongest spontaneous Raman bands have been observed, as exemplified by o-, m- and p- xylenes.
- 6) The number of degenerate vibrations is important in determining the SRS activity of that mode relative to other Raman bands. For instance, there are six C-H stretching vibrations in benzene whose frequencies are found as one strong band observed in the region $3000\text{--}3100 \text{ cm}^{-1}$. In comparison, monosubstituted benzenes have only five C-H stretching vibrations which did not appear in the

SRS although spectrum together with the predominant ring breathing vibration of benzene at $990\text{-}1010\text{ cm}^{-1}$ was observed.

- 7) Benzene vibrations at $\sim 1000\text{ cm}^{-1}$ are not good group frequencies for distinguishing mono-, di- and tri-substitution types. Nevertheless, in the SRS spectra of di- and tri-alkyl substituted benzenes, a strong band caused by the C-H stretch usually occurs in the range $2900\text{-}3000\text{ cm}^{-1}$
- 8) The position of an SRS peak is sensitive to the nature (e.g., electrophilicity) of the substituent groups as well as to their geometry in the molecule. For instance, the data collected on the carbon-halogen stretching frequencies in the SRS spectra of halogenated methanes, ethanes and ethylenes show that these vibrations are sensitive to: (a) the mass of the halogen atom, (b) the type of substitution (primary, secondary, or tertiary), and (c) the geometric arrangement of the molecule in the vicinity of the carbon-halogen bond.
- 9) SRS is lacking sufficient selectivity to discriminate among different liquid alcohols and esters. The difficulty encountered in the study of the spectra of hydroxylic compounds arises from the association of molecules through hydrogen bonding, which leads to an inhomogeneously broadened O-H stretch centered about $3300\text{-}3400\text{ cm}^{-1}$. As the half width of the band is about 200 cm^{-1} , its intensity is only 1/20 of the CH_3 and CH_2 stretchings. In addition, O-H bonds are weak Raman scatterers because their polarizability does not vary much with bond length. This Raman mode is so weak that it is not visible at all in the SRS spectrum; only the C-H stretchings are stimulated and amplified in intensity.
- 10) Compounds that are able to establish intermolecular hydrogen bonds (e.g.,

formaldehyde shown in Fig. 10(a) mostly have structured SRS peaks with a large width. On the contrary, compounds such as ethyl formate and ethyl propionate, which may have intramolecular hydrogen bonds as shown in Fig. 10(b), display a single peak in their SRS spectra.

- 11) There is a strong dominance effect when more than one SRS-active compound are present in the sample cell. The weaker SRS lines are usually inhibited by the stronger ones. This is probably a consequence of the depletion of pump laser radiation by the SRS activity of the strong lines [49].
- 12) No SRS activity is observed for the solutions of solid chemicals in water or organic solvents at those concentrations specified in Table 1. This may be ascribed to the concentration threshold which must be reached before the Stokes intensity grows efficiently from spontaneous Raman scattering [68].
- 13) The full widths at half maximum of SRS peaks are mostly $10\text{-}20\text{ cm}^{-1}$ for our experimental setup (except for those cases listed in parentheses in Table 1). This amount of SRS peak broadening is lower than that previously reported for organic liquids at room temperature [57]. It is mainly caused by stimulated Rayleigh wing scattering, which is a result of the reorientation and redistribution of anisotropic molecules induced by the pump laser field [69].
- 14) Specifically noteworthy in the spectral data is the exceptional SRS activity of hexafluorobenzene. There were six orders of observed Stokes shift which signify a very high gain for the multistage SRS process. This organic liquid has,

(a)

(b)

Fig. 10. Comparison between (a) inter-molecular hydrogen bond in formaldehyde and (b) intra-molecular hydrogen bonds in ethyl formate and ethyl propionate.

unfortunately, a refractive index of 1.37774 at 20°C. Hence it is not suitable for use in a hollow optical fiber to produce SRS radiation as a coherent light source in the visible and near infrared regions, unlike benzene, toluene and benzyl alcohol [69].

- 15) Multiple peaks were found to be characteristic of α -methylstyrene, cumene, butyl acetate, acrylonitrile, 2-methyl-2,4-pentanediol, formaldehyde, p-cymene, 4-chloro-o-xylene, 4-bromo-o-xylene, ethyl phthalate, formic acid, and 1-bromo-3-chloro pentane. Within the specified spectral range, these multiple peaks were strongly irreproducible in number, positions, and relative intensities from shot to shot. Appearance of multiple peaks in SRS had previously been explained by Colles using a model of parametric coupling of electric fields. These fields were locally induced by mechanical coupling among three molecules, two of which vibrated at one frequency and the third at another frequency [70]. Such peak multiplicity has some very important technological implications in the laser and optronics industry. When used in a liquid core optical fiber, they may constitute a continuous coherent light source for special applications, just like ethylbenzene with its exceedingly large SRS peak broadening [69].
- 16) It is equally interesting to see the SRS spectrum of malonaldehyde tetramethyl acetal shown in Fig. 11 which contains as many as eight distinct peaks between 2490 and 3390 cm^{-1} . These SRS peaks are equally spaced but they have dissimilar and asymmetrically distributed intensities. This molecule would be a very interesting subject for further study from the spectroscopic point of view in order to assign each of the eight peaks to different vibrational modes and to elucidate the mechanism of simultaneous stimulated scattering.

Fig. 11. SRS spectrum of malonaldehyde tetramethyl acetal which contains eight distinct peaks.

4.2 Internally Amplified SRS

The IASRS hypothesis theorized on p. 16 was tested using two model compounds (namely benzene and pyridine) which have exactly the same Raman shift. Pyridine served as the amplifier compound to provide the additional Stokes photons for stimulating a small population of benzene molecules to undergo SRS and be detected. In the absence of any amplifier compound, the intensity of the 1st-order Stokes shift of benzene was measured for different cell lengths while the pump laser intensity (I_p) was kept constant. The results in Fig. 12 show that changing the sample cell length from 2 cm to 5 cm reduced the concentration threshold noticeably. This verifies the general theory of SRS thresholds as indicated in Eq. 1. The concentration thresholds were at 26% and 7% benzene, respectively for a low laser energy of 0.1 mJ in the absence of any amplifier compound. No easy comparison can be made between the low and high I_p conditions because the measurements were taken on separate days. The standard deviation and hence the size of error bar for each datum point shown in Fig. 12 is smaller than the symbol used. Such as is the case for all other graphs throughout this thesis unless specified otherwise.

Similarly, the dependence of the 1st-Stokes intensity of benzene on its concentration (% by volume) in 2,2,4-trimethyl pentane (TMP) is shown as a standard calibration graph in Fig. 13. At a pump laser energy of 9 mJ, no SRS signal was observed for up to 7.4% benzene. This means that the gain of the sample was below the SRS threshold under the given experimental conditions. With an addition of 20% pyridine as an amplifier compound which generated additional Stokes photons to overcome the SRS threshold of benzene, a substantial increase in SRS sensitivity

Fig. 12. 1st-Stokes intensities ($I_s(r_1)=992\text{ cm}^{-1}$) versus benzene% in CCl_4 for different cell lengths and pump laser intensities. Focal length of lens = 10 cm.

Fig. 13. 1st-Stokes intensities for benzene in 2,2,4-trimethylpentane (TMP):
 (a) 0% pyridine, and (b) 20% pyridine. Pump laser energy = 9 mJ; cell
 length = 50 cm. Focal length of lens = 20 cm.

(as represented by the positive slope of the linear least-squares fit to the data) was observed for the same concentration range of benzene. An improvement in detection limit down to 0.34% benzene was thus realized (at three times the standard deviation of the blank). Note that the positive y-intercept of the standard calibration plot represents the background Stokes intensity produced by the amplifier compound itself. Our proposed physical model is that the amplifier molecules bridge the spatial gaps among the analyte (or benzene) molecules which are distributed distantly from each other throughout a dilute solution. As a result, Stokes photons can more effectively reach the next benzene molecules down the pump light path to sustain and amplify the desirable SRS process.

The upper limitation of IASRS sensitivity due to saturation in Stokes photon generation and its effect on detection limit were investigated. In an experiment using a higher laser energy of 18 mJ rather than 9 mJ used above, a larger y-intercept value (i.e., Stokes intensity as benzene % approached zero) was obtained from the standard calibration graph shown in Fig. 14. However, the slope (or SRS sensitivity) was decreased and the detection limit became 0.74% benzene which was approximately two times poorer than the 0.34% for 9 mJ. The decrease in SRS sensitivity can be attributed to saturation of the SRS signal at the high laser energy (or I_p). This kind of saturation should be avoided in analytical IASRS studies by choosing a low I_p or a low concentration of amplifier compound. The higher the laser energy, the smaller concentration of amplifier may be used so as to avoid unwanted, early saturation of Stokes photons generation which will lead to lower analytical sensitivity and nonlinearity in signal.

Fig. 14. 1st-Stokes intensities for benzene in TMP + 20% pyridine. Pump laser energy = 18 mJ.

Higher-Stokes SRS activities are occasionally found useful for the spectroscopic analysis of organic compounds present in complex mixtures. Amplification of the 2nd-Stokes line ($2s(\nu_2) = 3064 \text{ cm}^{-1}$) of benzene using 2nd-Stokes line of toluene ($2s(\nu_2) = 3078 \text{ cm}^{-1}$) is demonstrated in Fig. 15. The 2nd-Stokes intensity of benzene and the 2nd-Stokes intensity of toluene as a function of their individual % by volume in CCl_4 are represented by solid symbols in the centre and on the right of the graph (B and T, respectively). The trend of the solid triangles indicates that a concentration threshold might exist around 6% for the 2nd-Stokes SRS determination of benzene. Upon the addition of 17.5% toluene to the sample, however, benzene at concentrations below the previous threshold value could now be determined as evident by the open symbols for benzene + 17.5% toluene (B + T) on the left of the graph. These results verify once again our earlier hypothesis that an amplifier compound can be added to the analyte solution to augment the gain above the SRS threshold. This produces a measurable Stokes intensity and makes the determination of low analyte concentrations possible using higher-Stokes SRS activities.

IASRS may be applied to variety of applications such as environmental analysis in which a friendly compound (e.g., benzaldehyde) can be used as an amplifier compound to detect low concentrations of hazardous analytes (e.g., chlorobenzene). IASRS is a technique whose utility will be maximized when the analyte is toxic or costly compared to the amplifier compound. In cases where the analyte has a small gain factor relative to some $k'g_s$ contribution from a possible amplifier compound, the IASRS technique will also be found useful.

Fig. 15. 2nd-Stokes Intensities for (a) benzene ($2s(\nu_2) = 3064 \text{ cm}^{-1}$), (b) toluene ($2s(\nu_2) = 3078 \text{ cm}^{-1}$), and (c) benzene + 17.5% toluene ($= 3071 \text{ cm}^{-1}$) versus their % by volume in CCl_4 . Pump laser energy = 9 mJ.

The dependence of amplification coefficient (k' in Eq. 6) on the overlap of the analyte and amplifier SRS intensity profiles was evaluated numerically using Eq. 11. In these calculations, the analyte Stokes shift ($\omega_{R, \text{analyte}}$) was regarded constant while the amplifier Stokes shift ($\omega_{R, \text{amplifier}}$) was varied, and the same FWHM ($= 24 \text{ cm}^{-1}$) was given to both the analyte and the amplifier. Gaussian analyte and amplifier SRS intensity profiles for various $\omega_{R, \text{amplifier}} - \omega_{R, \text{analyte}}$ separations are shown graphically in Fig. 16(a). k' is maximum when the two Stokes shifts are identical in frequency ($\omega_{R, \text{amplifier}} - \omega_{R, \text{analyte}} = 0$) as can be seen in Fig. 16(b), other k' results were normalized to this maximum. When $\omega_{R, \text{amplifier}} - \omega_{R, \text{analyte}}$ increases from 0 cm^{-1} to 60 cm^{-1} , k' gradually decreases to zero.

If the analyte and amplifier have different FWHMs (or $\Delta\omega_R$ in Eq. 8), k' is still maximum when the two Stokes shifts are identical in frequency. Assuming equal gain factors for the analyte and the amplifier at the centre Stokes frequencies, larger k' values are expected at the wings for analytes with a larger FWHM (33 cm^{-1}) than that of the amplifier (24 cm^{-1}) as shown in Fig. 16(b), curve a. Conversely, smaller k' values are expected at the wings for analytes with a smaller FWHM (17 cm^{-1}) as shown in Fig. 16(b), curve c. When the centre frequencies differ (i.e., $\omega_{R, \text{amplifier}} - \omega_{R, \text{analyte}} > 0$), the same predictions can be made. The amplification coefficient will be enhanced by a larger FWHM which is associated with a higher degree of overlap between the analyte and amplifier intensity profiles. Note that in practice, an integrated effect of modified T_2 , λ_s^3 , $\Delta\nu_R$, and $d\sigma/d\Omega$ in a mixture of amplifier and analyte will be effective in the observed amplification.

(a)

(b)

Fig 16.

(a) Graphical illustration of amplifier and analyte SRS intensity profiles at various frequency separations. (b) Theoretical simulation of amplification coefficients versus the displacement of amplifier Stokes frequency from analyte's. Full width at half maximum for $a = 33 \text{ cm}^{-1}$, $b = 24 \text{ cm}^{-1}$, and $c = 17 \text{ cm}^{-1}$.

4.3 Effect of Temperature on Stokes Intensity

The gain factors of the 1st-order Stokes shift of benzene ($1s(\nu_1) = 992 \text{ cm}^{-1}$) calculated for different temperatures according to Eq. 2, 12 and 13 are plotted in Fig. 17. This theoretical graph illustrates that higher gain can be expected at lower temperature. At temperatures below 100 K, further reductions in temperature are not likely to improve the gain significantly because neither the Bose factor nor the Raman scattering cross-section ($d\sigma/d\Omega$) will change appreciably [48]. Above room temperature, on the other hand, the linewidth ($\Delta\nu_R = (\pi T_2)^{-1}$) of SRS modes in fact increases substantially with increasing temperature. The gain factor will decrease as a result of line broadening, causing further reduction in the SRS intensity.

An Abbe refractometer was used to measure the change in refractive index, n , with temperature of benzene (B), toluene (T) and 50% benzene in toluene (B+T). A reduction of 40 °C in temperature increased n by 1.4% for a liquid thickness of 0.1 mm as shown in Fig. 18. Therefore, the contribution of n to the variation of g_s becomes significant over a large temperature range.

The results of the temperature effect on the intensity of the Stokes signal from 50% benzene in toluene are shown in Fig. 19. The intensity of the SRS signal increased by a factor of 2.7 when the sample temperature was decreased from 21 to 10 °C only. A least-squares linear regression fit was attempted in Fig. 20 to characterize the trend of the data. The slope of the straight line was $-1429.9 \text{ counts } ^\circ\text{C}^{-1}$ with a correlation coefficient (R^2) of 0.985 over the relatively small temperature range studied. A calculation of temperature resolution ($=\text{standard deviation (SD)}/\text{slope}$) based on four measurements of 50% benzene in toluene was found to be 2.4 °C. This resolution is not

Fig. 17. Steady-state gain factor (g_s'') calculated for the first-order Stokes line of benzene (50% in toluene) as a function of temperature. The solid portion of the curve denotes the experimental temperature range examined in Fig. 18 and Fig. 19.

Fig. 18. Refractive index of benzene (B), toluene (T), and 50% benzene in toluene (B+T) versus temperature.

Fig. 19. 1st-Stokes intensity of 50% benzene in toluene versus temperature.

Fig. 20. 1st-Stokes intensity of 50% benzene in toluene versus temperature.

very high because of the intrinsically high fluctuations of Stokes intensity. Recognizing that the smallest measurable change in signal intensity using the specified PDA detector is approximately ten counts, we may conclude that a change of $7 \times 10^{-3} \text{ }^{\circ}\text{C}$ in temperature can possibly be determined in the ideal situation. The temperature effect on the intensity (as measured with a PMT) of 2nd-Stokes SRS shift for 50% benzene in toluene is shown in Fig. 21. Its general behaviour was found to be the same as 1st-Stokes shift shown in Fig. 20. Similarly, the temperature effect on the intensity of the 2928-cm^{-1} Stokes shift of ethanol is shown in Fig. 22, although the slope of the least-squares line is not the same as a different pair of compounds were involved. The liquid was actually flowing through the cell when the SRS intensities were measured. Furthermore, the extent of signal enhancement with decreasing temperature is so large that the technique holds promise for non-invasive thermometry in industrial process monitoring.

SRS thermometry offers better sensitivity at a higher number density of molecules (N) for the same magnitude of temperature change. This follows from the first derivative of Eq. 1, where I_p and z are held constant. The relative change in I_s may be expressed by

$$\frac{dI_s}{I_s} = zI_p dg_s \quad (14)$$

Assuming T_2 (or $\Delta\nu_R$) is constant as a first approximation, the first derivative of g_s with respect to T can be acquired from Eq. 2, 12 and 13:

Fig. 21. 2nd-Stokes (3071 cm^{-1}) intensity of 50% benzene in toluene versus temperature.

Fig. 22. 1st-Stokes (2928 cm^{-1}) intensity of flowing ethanol versus temperature.

$$dg_s = \frac{-2\alpha\beta N}{T^2 \exp(\beta/T)} dT \quad (15)$$

where

$$\alpha = \frac{8\pi c_0^2}{\hbar n_s^2 \omega_s^3 \Delta \nu_R} \frac{d\sigma}{d\Omega} \quad \text{and} \quad \beta = \frac{\hbar \omega_R}{k_B}$$

Substituting dg_s from Eq. 15 into Eq. 14 will yield

$$-\frac{dI_s}{I_s} = 2zI_P \alpha \beta N \frac{dT}{T^2 \exp(\beta/T)} \quad (16)$$

Eq. 16 indicates that the relative change in SRS intensity (i.e., $-dI_s/I_s$) with differing temperature is a function of N and T . In other words, the sensitivity of SRS thermometry scales linearly with N and non-linearly with T . As shown in Fig. 23, $-dI_s/I_s$ increases directly with increasing percentage of benzene in toluene at any given temperature. Since the ability of SRS as a remote sensing method has been established in our research laboratory, this technique should be useful for real-time temperature monitoring of hard-to-reach areas such as those found in industrial plants. The laser pulses may be carried to the sampling sites using fibre optics. The most SRS-active and most concentrated component is then optically pumped (i.e., excited) to generate an SRS signal amplitude for correlation with the sample temperature. Obviously it would be ideal if the solvent, which is the bulk component (with the largest possible value for N) of any chemical system, is SRS-active so that it can serve as an internal temperature sensing element. As shown in Tables 1 and 5, many common organic solvents are known to have a sufficiently high g_s value for this purpose.

The fact that much higher sensitivity ($-\Delta I_s/I_s$ in Fig. 23) can be attained at

Fig. 23. Sensitivity of SRS thermometry (or $-\Delta I_s/I_s$) versus temperature for (a) 10%, (b) 50%, and (c) 100% benzene in toluene.

elevated temperatures promises application of SRS thermometry to high-temperature reactors (up to the boiling point of the solvent under high pressure), without any potential problem of chemical or physical corrosion with conventional temperature probes. However, as the SRS gain (see Fig. 17) decreases rapidly in the high-temperature range, the low intensity of SRS radiation cannot be measured by an ordinary PDA system which is suited to applications involving medium to high light levels typically being 2000-3000 photons/count. Consequently, a combination of a high-gain microchannel plate intensifier and a low-readout-noise PDA detector will be required to improve the detection sensitivity for low-light-level response. Alternatively a PMT may be used as a highly sensitive detector in the SRS setup to improve the thermometric sensitivity at high sample temperatures. As long as the SRS intensity level is kept within the dynamic range of the optical detector, utilization of a more sensitive detection system always provides the power to measure smaller changes in absolute light intensity.

It was noticed in our experiments that the FWHM of the benzene 1st-Stokes SRS peak decreased by 1.9% when the temperature was lowered by 10 °C. Reduction in linewidth is the direct consequence of reducing inharmonic damping contributions to a specific Raman mode. Lowering the sample temperature slows down the molecular motion and reduces the number of collisions in each unit volume. As a result, the possibility of collisional deactivation of excited molecules is decreased. Theoretically, the linewidth is reduced upon cooling by a factor corresponding to the increase in SRS gain. This is due to the fact that, according to Eq. 2, g_s is inversely related to $\Delta\nu_R$ [30]. Most of the high-resolution investigations by other laboratories in the last decade to study the temperature dependence of the Raman intensity were also achieved on SRS

spectrometers, because the SRS spectrum could be obtained when the sample temperature changes without distortion as in spontaneous Raman spectroscopy. Applications of temperature measurements to combustion media in engines and reactors had focused on molecular nitrogen because of its simple spectroscopic properties [71]. Collisional broadening coefficients of the nitrogen Q-branch were accurately measured in the temperature range 295-1310 K on an SRS spectrometer. The results were in good agreement with the values determined from semi-classical calculations.

4.4 Optimization of Experimental Parameters

4.4.1 Cell Position

The position of the sample cell (front window) with respect to the focusing lens (focal length = $f = 10$ cm) had a great effect on the forward-scattered 1004-cm^{-1} Stokes intensity of neat toluene. As shown in Fig. 24, for a 5-cm-long cylindrical cell, the highest SRS intensity was obtained at an optimum position of 7.0-7.5 cm from the focusing lens. For a 10-cm cell, the highest SRS intensity was obtained at ~ 6.0 cm. No changes in the line shape or the Stokes shift were observed when the cell position was altered. Such discrepant behaviour can be explained by the fact that the confocal volume (i.e., SRS active zone estimated to be ± 0.5 cm about the focal point) was at the middle of the 5-cm cell when the cell position was at 7-8 cm. Hence the corresponding Stokes intensity was maximum. For the 10-cm cell the confocal volume of the laser beam was

Fig. 24. 1st-Stokes intensity of toluene ($1s(\nu_1) = 1004 \text{ cm}^{-1}$) versus cell position (or distance of front window from the focusing lens) for a 5-cm and a 10-cm cylindrical cells. Focal length of lens = 10 cm.

at the middle of the cell when the cell position was at 6-7 cm to produce the maximum Stokes intensity. As the cells were moved away from the optimum positions, the confocal volume was dragged out of the cell and the SRS intensity quickly fell towards zero.

The back-scattered SRS Stokes intensities for water as a blank (at 992 cm^{-1}) and a 33% aqueous solution of pyridine (at $1s(\nu_1)=992\text{ cm}^{-1}$) in a 50-cm cell were also measured for various distances of cell (front window) from the focusing lens ($f = 48\text{ cm}$). No variation in the Stokes intensity was observed over the range of 17.5-32.5 cm, as shown in the top part of Fig. 25. As long as the confocal volume (and hence the SRS active zone) was placed inside the cell, the Stokes intensity would not be affected by the exact position of the confocal volume (i.e., the distance of the cell from the focusing lens). This result implies that, in a focused beam configuration, SRS occurs within the confocal volume where the photon flux (or laser power density) is the highest and sufficiently large to induce the stimulation process. This may be regarded as an advantage of SRS in analytical measurements where there is no need for precise optimization of the cell position if a relatively long cell is used. Furthermore, the confocal volume may be located at different points inside a large-volume sample to determine the distribution of analyte concentrations. Next, the applied voltage to the PMT (see Fig. 8) was decreased from 600 V to 450 V and the measurements were repeated to ensure that the lack of changes in Stokes intensity was not due to detector output signal saturation. As evident from the bottom part of Fig. 25, the same trend was observed again to verify the confocal volume hypothesis. This is in agreement with a previous report that the gain for a backward Stokes waves was independent of the pump

Fig. 25. 1st-Stokes intensities of water and 33% pyridine ($1s(\nu_1)=992\text{ cm}^{-1}$) versus position of 50-cm cylindrical cell for two different PMT applied voltages. Focal length of lens = 48 cm.

confocal length position when the confocal length was much smaller than the cell length [15].

4.4.2 Cell Length

The dependence of Stokes intensity on sample cell length was also investigated. The use of a 10-cm cell effectively doubled the intensity in comparison with a 5-cm cell, as evident in both Fig. 24 and 26. When the 5-cm cell was added to the 10-cm cell in series, the combined cells (15 cm in total length) did not increase the Stokes intensity any further. As explained above, the SRS process occurs in the confocal volume. While the confocal volume might not be totally accommodated inside the 5-cm cell, it was well accommodated by the 10-cm cell. Obviously, further increase in the cell length beyond the confocal volume would not increase the SRS intensity.

4.4.3 Focusing of Laser Beam

With a focusing lens standing in its path, a collimated laser beam will focus to a minimum focused spot called the waist at the focal point. For a laser beam with a Gaussian intensity profile, the effective radius of beam waist, ω_0 , is proportional to the focal length, f , of the focusing lens [72]:

$$\omega_0 = \frac{\lambda_p f}{\pi \omega_1} \quad (17)$$

where λ_p and ω_1 are the pump laser wavelength and the unfocused laser beam radius, respectively. The distance along the beam from the waist to where the curvature is maximum, the area doubles and the divergence asymptotically approaches linearity is:

Fig. 26. 1st-Stokes intensity of toluene ($I_s(\nu_1)=1004\text{ cm}^{-1}$) versus sample cell length measured using the optimum cell position. Focal length = 10 cm.

known as the Rayleigh range or confocal length, z_R :

$$z_R = \frac{\pi \omega_o^2}{\lambda_p} \quad (18)$$

At the beam waist the laser energy density is maximum and hence most of the initial Stokes photons are generated there. Therefore, in the forward-scattered SRS measurements (see Fig. 24), it is probably the second half of the confocal length (after the focal point) that may be considered the active SRS zone. In a small cell length of 5 cm, the 2nd-half of z_R should be located close to the front window in order to produce the maximum possible SRS intensity. Through Eq. 17 and Eq. 18, a long-focal-length lens may be used to increase the confocal length and hence the number of Raman scatterer molecules in the confocal volume. Changing the focusing lens from $f = 5$ cm to $f = 10$ cm doubles the ω_o of the focused spot and hence increases z_R by a factor of 4. In fact, the confocal volume ($\approx \omega_o^2 z_R$) increases as the fourth power of the focal length. Previously, the SRS data for high-efficiency backward Stokes Raman conversion in deuterium showed that longer focal lengths produce higher conversion efficiencies [73]. Ultimately, no focusing lens should be used in the collimated beam configuration [63] in order to provide the full cell length for use as the effective z_R . In terms of laser energy, however, a much higher energy (typically 30 mJ) is required for performing SRS in a collimated beam configuration whereas in a focused beam configuration lower laser energies (typically 1-10 mJ) can be used.

Consequently, if a sample cell with a length L much greater than z_R is used, the SRS intensity is independent of the z_R position in the cell. If L and z_R are comparable, the SRS intensity will be affected by the z_R position, as set by the cell distance from

focusing lens.

4.4.4 Slit Width

The slit width, which determines the effective band-pass of the monochromator, was optimized for the best S/N before the SRS intensity was measured using setup 2 for low analyte concentrations. It was varied from 5 μm , 25 μm to 100 μm and the intensity of the 2nd-order Stokes line of benzene ($2s(\nu_1)=2\times 992\text{ cm}^{-1}$, arbitrarily chosen) was measured. The highest S/N was obtained for a slit width of 25 μm , as shown in Fig. 27. At the larger slit width of 100 μm , a slightly lower S/N was obtained, mainly because of a higher noise level due to more stray light entering the monochromator.

4.4.5. Signal Integration Time

One of the interesting features of SRS is the macroscopic statistical fluctuations of the Stokes radiation. Taking the natural logarithm of Eq. 1 yields

$$\text{Ln}I_s = \text{Ln}I_{s(0)} + g_s I_p z = \text{const.}$$

which implies that for an SRS-active compound (with given g_s and $I_{s(0)}$), a constant pump laser intensity (I_p) and the same interaction length (z), $\text{Ln}I_s$ should be theoretically constant. In reality, however, $\text{Ln}I_s$ fluctuates significantly during the course of a single SRS measurement. In order to investigate the dependence of Stokes intensity fluctuations on pulse-to-pulse variation in pump laser intensity, both the Stokes and the laser intensities were measured simultaneously for neat benzene versus time. As shown in Fig. 28, the $\text{Ln}I_s$ and I_p collected from 31 accumulated PDA spectra versus time indicate that, with few exceptions, the fluctuations in $\text{Ln}I_s$ were associated with the pulse-to-pulse

Fig. 27. 2nd-order Stokes ($2s(\nu_1)=2\times 992\text{ cm}^{-1}$) intensity of 55% benzene in CCl_4 and its signal to noise ratio, as a function of slit width. Cell length = 10 cm.

Fig. 28. $\text{Ln}(\text{Stokes intensity})$ and pump laser intensity versus time.

A resolution test chart featuring various patterns of horizontal and vertical lines. The patterns are arranged in a grid-like fashion, with some patterns labeled with numbers such as 1.0, 1.1, 1.25, 1.4, 1.6, 1.8, 2.0, 2.2, 2.5, 2.8, 3.2, 3.6, 4.0, 4.5, 5.0, 5.6, 6.3, 7.1, 8.0, 9.0, 10.0, 11.2, 12.5, 14.0, 16.0, 18.0, 20.0, 22.5, 25.0, 28.0, 32.0, 36.0, 40.0, 45.0, 50.0, 56.0, 63.0, 71.0, 80.0, 90.0, 100.0, 112.0, 125.0, 140.0, 160.0, 180.0, 200.0, 225.0, 250.0, 280.0, 320.0, 360.0, 400.0, 450.0, 500.0, 560.0, 630.0, 710.0, 800.0, 900.0, 1000.0, 1120.0, 1250.0, 1400.0, 1600.0, 1800.0, 2000.0, 2250.0, 2500.0, 2800.0, 3200.0, 3600.0, 4000.0, 4500.0, 5000.0, 5600.0, 6300.0, 7100.0, 8000.0, 9000.0, 10000.0. The patterns consist of horizontal and vertical lines of varying thicknesses and spacings, used to test the resolution capabilities of imaging systems.

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

variation in I_p when the integration time was 0.02 s. The magnitude of fluctuations in Stokes intensity is determined by the statistical nature of the SRS process which arises from quantum noise being amplified to macroscopic levels [74].

In order to average out unstable SRS signals, particularly those small ones obtained from relatively low analyte concentrations, a long integration time (~ 1 -2 min) was necessary. The steady-state variations in intensity of the 2nd-Stokes shift of benzene, $2s(\nu_1)$, are illustrated in Fig. 29 for two different concentrations ($a = 53\%$ and $b = 76\%$) in CCl_4 using an integration time of 0.66 s. While the peak intensity was fairly constant at the higher concentration, it fluctuated significantly at the lower one. These results are in agreement with the work of Grabchikov et al [74]. They observed a change in the statistics of the energy of Stokes pulses at various conversion efficiencies (or g_s). Their smallest value for standard deviation in high conversion-efficiency measurements was 4%. For long integration times, saturation of the detector occurs easily and must be prevented by a reduction of stray light. The detector noise must also be minimized by using both thermoelectric and water cooling of the PMT or PDA head down to -35°C . Moreover, the number of accumulated spectra for summation should be maximized in order to obtain the largest possible S/N within practical analysis time limits.

4.4.6 Flow Velocity of Sample

The effect of sample flow velocity on the 1st-Stokes (2928 cm^{-1}) intensity of ethanol in a 30-cm cell at room temperature was also investigated. The results in Fig. 30 reveal that changes in flow velocity from 0 to 5.5 m s^{-1} had no effect on the SRS

Fig. 29. 2nd order Stokes intensity versus time for (a) 53% and (b) 76% of benzene in CCl_4 . Slit width = $25 \mu\text{m}$.

Fig. 30. 1st-Stokes intensity of ethanol versus flow velocity.

intensity of ethanol. The RSD of all data points ($= 0.8\%$) was less than the 1.1% RSD for each individual datum point as shown in Fig. 30.

4.5 Effect of Absorbing Substances on Stokes Intensity

The effect of pump laser attenuation due to absorbing substances on the 1st-Stokes intensity of benzene (50% in toluene by volume) was studied using 0.01 M azulene in isopropanol as a model absorbing compound. Azulene (C_{10}H_8 , cyclopentane-cycloheptane) is an organic dye molecule [75] which absorbs in the visible region. As shown in Fig. 31, Stokes intensity decreased as the concentration of azulene was increased in the 10-cm sample cell. For a 15-fold increase in azulene concentration, the Ln (Stokes intensity) decreased by a factor of 38. This reduction in Stokes intensity due to the absorption of laser light by azulene could interfere with analytical measurements unless the method of standard addition is employed to calibrate the system response.

4.6 Saturation and Linear Dynamic Range

As I_p is increased, I_s grows exponentially from spontaneous Raman scattering up to the point of saturation. At high I_p , the first-order SRS Stokes intensity becomes laser-power independent [24,26,59], which is caused mainly by cascaded depletion of the 1st-order Stokes line to generate 2nd and higher-order ones and partly by self-focusing [21]. Similar behaviour was observed when I_s was measured with increasing benzene concentration in CCl_4 (Fig. 32). The successive depletion of Stokes lines is apparent when saturation of the 1st-order Stokes line began concurrently with a growth of the 2nd-order Stokes line, and so on for the 3rd-order Stokes line.

Fig. 31. 1st-Stokes intensity of 50% benzene in toluene versus azulene concentration in solution.

Fig. 32. Intensity of the 1st, 2nd and 3rd-order Stokes lines versus benzene% in CCl₄ at relatively low pump power.

In order to extend the linear dynamic range of the technique for high-concentration analytical applications, the problem of saturation must be avoided. This could be achieved if the laser power and/or interaction volume were decreased. Fig. 12 shows the 1st-order Stokes intensity measured for various benzene % in CCl_4 . The results indicated that a high I_p could induce early signal saturation even at relatively low concentrations. A greater linear dynamic range was achieved with the use of a lower I_p . In addition, the cell length was changed to be 2 cm which was shorter than the self-focusing threshold length in order to impede large-scale self focusing (which would cause early depletion of Stokes intensity). Consequently, a linear dynamic range of 20-100 % benzene was attained.

4.7 SRS Sensitivity and Limits of Detection

Several model compounds were previously chosen by Lai and Harris [63] for quantitative SRS studies with a collimated beam configuration. The concentration dependence of the SRS intensity for acetone in water at a Stokes shift of 2921 cm^{-1} , benzene in tetrahydrofuran (THF) at 992 cm^{-1} , cyclohexane in CCl_4 at 2852 cm^{-1} , and ethanol in water at 2928 cm^{-1} were determined using an excitation energy of 36 mJ per pulse. Their results are summarized in Table 2. Some calculated values for the limits of detection in a 50-cm-long cell are also included.

Table 2. Typical SRS limits of detection for organic compounds using a collimated beam configuration.

Compounds	Limits of Detection (% by volume)	
	(10-cm cell)	(50-cm cell)
Acetone in water	0.0007	0.00015*
Benzene in THF	0.4	0.085
Cyclohexane in CCl ₄	19	4*
Ethanol in water	0.1	0.02*

* Calculated values

In our work, a focused beam configuration was employed for the benefit of a lower energy requirement. The concentration dependence of the SRS intensity for benzene in CCl₄, benzene in THF using IASRS, pyridine in water, pyridine in THF were all determined at a Stokes shift of 992 cm⁻¹ at room temperature. Their results are summarized in Table 3, together with that for toluene in CCl₄ determined at a Stokes shift of 1004 cm⁻¹.

The back-scattered setup 4 shown in Fig. 8 was used for the determination of pyridine in water and THF. As all of the optical components are set up on one side of the sample cell, this configuration is promising for process stream monitoring purposes in industrial plants. It is beneficial in terms of residual laser light rejection compared with the forward scattered setup (see Fig. 4 and 5) used for the determination of other compounds. It also offers higher SRS collection efficiency due to a wider possible aperture which eliminates fluctuations due to laser pointing errors.

Table 3. Typical SRS concentration thresholds for organic compounds using a focused beam configuration.

Compounds	Concentration Thresholds (% by volume)		Experimental	
	(10-cm cell) f = 10 cm	(50-cm cell) f = 20 cm	Laser Pulse Energy (mJ)	Setup
Benzene in CCl ₄	7	9 ¹	0.1 ²	1
Benzene in isopropyl alcohol	13.5		0.1	2
Benzene in TMP + 20% pyridine	0.034		9	2
Benzene in toluene		38 ¹	0.1 ²	1
Pyridine in water		6.8	10	4
Pyridine in THF		13.1	10	4
Toluene in CCl ₄		13.2 ²	0.1 ²	1

¹ The 2nd-Stokes lines are used.

² Setup 1 is used with $\lambda_p = 500$ nm.

Since the SRS intensity scales exponentially with the number density of molecules (N), in accordance with Eqs. 1 and 2, a 25-fold decrease in N will cause the SRS intensity to reduce by a factor of 7.2×10^{10} . As a result, the analytical signal diminishes rapidly at low analyte concentrations. Ultimately, the generation and detection of SRS radiation will be limited by the existence of a threshold concentration (which depends on $d\sigma/d\Omega$ through g_s). Below the threshold, the Stokes radiation will drop to the background level of spontaneous Raman scattering. When the SRS intensity becomes weak with decreasing analyte concentration, minimization of signal loss in the measurement system will help improve the limit of detection. Gratings have the known disadvantage of producing greater amounts of stray radiation as well as reflection losses [76]. Hence,

the use of two optical band-pass filters and two HNFs instead of a monochromator was evaluated as an alternative wavelength isolation device to monitor one specific compound at a time with a PMT detector in quantitative measurements. The background signal due to solvent SRS radiation may be effectively rejected by the use of a HNF designed for the solvent SRS frequency. In the focused-beam configuration, the SRS activity occurs mainly within the confocal length of the focusing lens in the sample cell where the laser energy density is high and the deposited heat may be great. Hence, the laser beam might be deflected due to the large magnitudes of local temperature and refractive index gradients when the detector is about 3 m away from the cell (i.e. ≥ 50 cm). When the back-scattered SRS radiation was measured using setup 4, the problem of laser beam deflection no longer was observed since the detection system was located as close as 30 cm to the sample cell.

The primary difficulty with the SRS technique is the Rayleigh and background SRS activity of solvent that accompany intense laser radiation. Relative to the SRS signal at low analyte concentrations, the background solvent SRS radiation can be enormous, obliterating much of the spectrum. Even if one could observe the analyte SRS spectrum superimposed on the background, the noise contribution of the background solvent SRS radiation degrades the analyte S/N of the SRS peaks. Also, liquid samples must be free from dust particles or emulsions; otherwise the SRS spectrum may be masked by Tyndall scattering. These represent some shortcomings of the SRS technique.

The conversion of pump laser light to Stokes radiation depends upon the magnitude of g_s . As listed in Table 5, the g_s values clearly lie between 1×10^{-10} cm W⁻¹

compounds exhibit similar SRS sensitivities which differ from each other by no more than two orders of magnitudes. Under the assumption of equal background noise across the Raman shift region, the SRS detection of benzene will exemplify the better of those for most other compounds, all within two orders of magnitudes.

As explained in section 4.2, IASRS is useful in the determination of chemicals at concentrations below their thresholds. The benefit of working at low temperatures is twofold. It not only increases the gain factor and hence SRS intensity but also alleviates the fluctuations in Stokes intensity as expressed by the RSD. For a solution of 50% benzene (by volume) in toluene the RSD of the 2nd-Stokes intensity in four measurements could be lowered (from 7.7% to 3.1%) by reducing the sample temperature from 5°C to -15°C. At the same time, the 2nd-Stokes intensity increased by a factor of 5. Therefore, the S/N (and detection limit) would be increased 12-fold ($= 2.4 \times 5$).

The Stokes intensities of neat benzene and a 10% solution (by volume) of benzene in 2,2,4-trimethyl pentane (TMP) were measured employing setup 2 in order to determine the RSD's at two concentrations using the peak heights of 31 spectra. RSD is a good indication of the extent of fluctuations in SRS Stokes intensity. The RSD of the Stokes intensity for neat benzene was 8.62% at a laser energy of 2.8 mJ and integration time of 0.02 s. At a higher laser energy of 6.4 mJ, the RSD was 5.3% which suggests that the 1st-Stokes intensity was saturated due to depletion of laser light into higher-order Stokes radiation. Up to 4 orders of Stokes shifts were observed at the laser energy of 6.4 mJ.

At a concentration of 10% benzene (by volume) in TMP, the RSD of the Stokes

intensity was found to be 12.5% which is greater than the corresponding RSD for neat benzene ($=8.6\%$) at a laser energy of 2.8 mJ. These measurements corroborate with the theory of SRS which says that the sensitivity of SRS measurements increases with increasing analyte concentration, up to the point of saturation due to depletion of incident laser light [63]. In other words, the higher the analyte concentration, the more discriminating the technique is to small changes in analyte concentration. Such enhanced discriminating is not afforded by other spectroscopic techniques which generally show a constant sensitivity throughout the linear dynamic range. This unique characteristic of SRS could be valuable in situations where the exact concentration of a major constituent in the sample must be determined to a high degree of precision.

Various techniques may be proposed for improving the SRS sensitivity for compounds in solution. These techniques for enhancing the measured SRS intensity fall into several categories. In the absence of a concentration threshold, the sensitivity of an SRS measurement depends upon the laser intensity and its stability, excitation frequency, collection efficiency, as well as background SRS activity and fluorescence of the solvent. First, the limit of detection can be improved by increasing the SRS efficiency. The pump laser energy may be increased to provide a higher I_p . This approach will ultimately be limited by the damage thresholds of the liquid sample and optical components. Second, a key factor in successful trace-level SRS analysis lies in the elimination of stray light, background signals, dark current level and their proportional noise. Further extension of the detection sensitivity can be attained using a higher interaction volume to sample a larger number of scatterers, which is provided by a greater cell length, a longer focal length lens and/or a multipass cell configuration (see

Fig. 9). For solutions, a lower concentration can be determined if a larger volume is probed, assuming the detection limit is determined by the absolute number of scatterers monitored by the spectrometer. An example of this approach is the optical waveguide of Walrafen [77], where the sample was placed in a hollow optical fibre which conducted the laser beam down its bore. Enhancements in sensitivity by a factor of 100 to 1000 and some new spectral features for benzene and tetrachloroethylene were observed [78]. Unfortunately, the generality of the approach is limited by the requirement that the sample liquid have a higher refractive index than the fibre material ($n=1.45-1.60$). This constraint excludes all aqueous samples and most organic liquids. A similar approach with a Teflon tube ($n=1.35$) has been attempted, but optical losses were high [79].

A long cylindrical glass tube, which constrains the laser beam and spontaneous Raman scattering to a large sample volume (and therefore more scatterers) by internal reflection, may also increase the sensitivity by a factor of 30 to 50. Unlike previous approaches there are no constraints on the refractive index of the sample solution, because the waveguide is formed at the air/glass rather than glass/solution interface. This approach enhances sensitivity while retaining the remote sensing capability and low radiation density at the sample and in the spectrometer [79].

A more efficient detection of the SRS emission generated from the sample will increase the sensitivity of the SRS spectrometer. PDA detectors have an advantage over PMT-based instrumentation of real-time multichannel measurements of full spectra. However, these detectors suffer from relatively high detector noise and dark current levels. Another type of array detector, the charge-coupled device (CCD) detector, shares the same multichannel advantages as the PDA detector [80] and could better serve the

Fig. 35. FT-IR spectrum of the same multicomponent mixture as used in Fig. 34.

toluene. For instance, benzene in toluene was determined using the intensity of its 2nd-order Stokes line as shown in Fig. 33. The linear dynamic range was observed to extend from 40% to 90% benzene.

The SRS spectrum of benzene at high I_p ($\lambda_p = 532$ nm) exhibits a 1st-order Stokes peak at 562 nm (corresponding to the 992 cm^{-1}), a 2nd-order Stokes peak at 595 nm (corresponding to $2 \times 992\text{ cm}^{-1}$), and a 3rd-order Stokes peak at 632 nm (corresponding to $3 \times 992\text{ cm}^{-1}$). The spectrum shows that although the fundamental peak of benzene at 562 nm overlapped the second harmonic peak of CCl_4 , the 2nd-order Stokes peak of benzene at 595 nm could be used for quantitative analysis as it is not interfered by any solvent peak signals. The SRS determination of benzene (1.0% to 9.1% benzene by volume) in CCl_4 using the 2nd-order Stokes peak of benzene was demonstrated by Lai and Harris [63]. No concentration threshold was apparent at a laser pulse energy of 29 mJ. The 2nd-order Stokes lines of several compounds listed in Table 1 and Table 5, Appendix II may be useful for the quantitative analysis of their binary mixtures with other organic compounds (such as benzene in ethylbenzene).

The competition between different vibrational Raman transitions at various sample temperatures may lead to the observation of different orders of SRS lines or changes in Raman shifts [46]. Such characteristics may also be utilized in qualitative and quantitative works to differentiate between chemicals with overlapping 1st-order SRS peaks.

Fig. 33. Intensity of the 2nd-order Stokes ($2s(\nu_1) = 2 \times 992 \text{ cm}^{-1}$) line versus benzene% in toluene at low pump power.
Cell length = 10 cm, focal length of lens = 10 cm.

4.9 Qualitative Analysis of Multicomponent Mixtures

A qualitative analysis of a multicomponent mixture in a 30-cm-long sample cell was carried out to demonstrate the ability of SRS as a useful technique for discriminating among different classes of Raman-active compounds in a mixture. The SRS spectrum for a mixture of carbon disulfide (8%), cyclohexane (34%), tetrachloroethylene (48%), and benzene (10%) was recorded and displayed in Fig. 34. The spectrum includes a strong peak at 656.5 cm^{-1} for 8% CS_2 , a fairly weak peak at 801 cm^{-1} for 34% cyclohexane, a 2nd-order Stokes peak at $2 \times 446.9\text{ cm}^{-1}$ for 48% tetrachloroethylene, and a peak at 992 cm^{-1} for 10% benzene. These model compounds have different chemical bonds such as C=S, C-C, C-Cl, and C=C which gave rise to the specific Stokes shifts. Their Stokes frequencies are therefore a good indication of the different kinds of compound classes present and may be found useful in the qualitative analysis and screening of multicomponent mixtures.

An FT-IR spectrum of the above mixture was recorded using an FT-IR spectrophotometer (Perkin-Elmer model 1600, Norwalk, Connecticut, U.S.A.) to compare with the SRS spectrum in terms of their ability in discriminating among the mixture components. In the FT-IR spectrum shown in Fig. 35, the most concentrated components of the mixture (i.e., tetrachloroethylene at 910.5 and 777.4 cm^{-1} and cyclohexane at 1449.7 and 2927.3 cm^{-1}) have strong IR absorption while the CS_2 at 1524.6 cm^{-1} and benzene peaks at 1478.8 and 3035.7 cm^{-1} have very weak absorption. This is the opposite of what was observed in the SRS spectrum of the mixture. Hence, as expected from the general theory of IR and Raman spectroscopies, it may be concluded that SRS and FT-IR are two complementary techniques for the analysis of

Fig. 34. SRS spectrum of a multicomponent mixture containing 8% carbon disulfide, 34% cyclohexane, 48% tetrachloroethylene, and 10% benzene.

Fig. 35. FT-IR spectrum of the same multicomponent mixture as used in Fig. 34.

organic compounds in a multicomponent mixture. Compounds which are highly SRS active would exhibit weak FT-IR absorption, and vice versa.

The SRS spectrum of a different mixture containing carbon disulfide (8%), cyclohexane (28%), tetrachloroethylene (52%), and benzene (12%) was recorded and shown in Fig. 36. The Stokes peak for CS_2 was reduced in intensity while the cyclohexane and benzene peaks grew substantially as compared with Fig. 34. No change was observed in their Stokes frequencies. Neat tetrachloroethylene has a SRS Stokes shift centred at 446.9 cm^{-1} which sometimes appears as triplet. However, the 1st-order Stokes shift was not observed due to dominance effect of the other compounds. The drastic intensity changes between Fig. 34 and 36, which resulted only from slight modifications in the component concentrations, is worthy to note. These changes in Stokes intensities were not proportional to the changes in chemical composition. This observation implies that the Stokes intensity scale (or its natural logarithm) may not be useful for quantitative determination of compounds in a mixture. If the Raman scattering cross section of one compound (e.g., benzene) is relatively high, its Stokes intensity may dominate over the other Stokes intensities. The latter may become either weak or totally missing as was the case for tetrachloroethylene in Fig. 36. At low analyte concentrations the dominance effect due to the solvent is also only observed. For a 25% solution of ethanol in water, no SRS activity was observed from water while the SRS band of water was very strong at low concentrations of ethanol. The same dominance effect was observed for benzene and CCl_4 . In a 1:1 mixture, no SRS peak was observed for CCl_4 . Intermolecular energy transfer [83,84] may also have been involved in the changes in SRS intensity of benzene and cyclohexane in the mixtures. This will need detailed

Fig. 36. SRS spectrum of a multicomponent mixture containing 8% carbon disulfide, 28% cyclohexane, 52% tetrachloroethylene, and 12% benzene.

investigation by molecular spectroscopists.

Different laser energies may be used to screen for compounds with different gains or Raman scattering cross sections. As shown in Fig. 37, at relatively low laser power (or oscillator energy ≤ 615 V), highly SRS-active components such as benzene first show up in the SRS spectrum. At higher laser powers (or oscillator energy ≥ 645 V), the less SRS-active components will eventually appear. Hence, depending on the kinds of compounds that are present or to be determined, the laser energy may be tuned in analytical SRS measurements to exhibit strong SRS signals while still hiding relatively weak signals under their concentration threshold.

4.10 Screening of Wines and Liquors for Alcohol Content

SRS may be used to differentiate between white wines with low and high alcohol contents in their original transparent or coloured glass bottles. A bottle (green glass) of white wine with 10.5% by volume of alcohol and a diameter of 11 cm (Edelwine, Cartier Wines & Beverages, Niagara Falls, Canada) was put, instead of the regular cylindrical sample cell, in the SRS spectrometer (setup 2, Fig. 6). Its SRS spectrum was recorded with a laser energy of 19 mJ and is shown in Fig. 38(a). There is a small peak at 2928 cm^{-1} due to ethanol C-H vibrational mode and a very strong water peak centred at 3409 cm^{-1} due to different O-H vibrational modes of water.

Two clear bottles of vodka (diameter = 8 cm, Ste Pierre Smirnoff Fls., Toronto, Canada) and 12-year-old whisky (diameter = 7.5 cm, Chivas Regal, Chivas Brothers Ltd., Scotland), both with a 40% ethanol content, were placed separately at the sample cell position in the spectrometer to obtain the SRS spectra shown in Fig. 38(b) and 38(c),

Fig. 37. SRS spectra of a multicomponent mixture (same as Fig. 34) measured at different laser energies.

Fig. 38. SRS spectra of (a) 10.5% alcohol content wine, (b) 40% alcohol content Vodka, and (c) 40% alcohol content Whisky, all contained in their original bottle.

respectively. The ethanol SRS peak was so intense that it saturated the PDA detector at the operating laser energy of 19 mJ. When, the laser energy was lowered to ~ 4 mJ the corresponding spectrum was collected without overshooting the Stokes intensity scale. No SRS signal for water was observed at either the high or low energy for the liquors with a 40% alcohol content. The gain factor ($= 5.1 \times 10^{-1}$) of ethanol is 51 times greater than that for water ($= 1 \times 10^{-1}$) as listed in Table 5, Appendix II. Hence, at the high ethanol concentration, the laser light was depleted into the SRS line of ethanol and no water SRS peak could be produced.

In summary, the alcohol content of a bottle of wine or liquor may be qualitatively examined by looking at the SRS spectrum without sampling or other pretreatment procedures. Quantitative determination of ethanol content may also be performed by comparing the area of the ethanol peak with a series of ethanol calibration standards. This new analytical technique should be desirable with customs offices where numerous bottles must be screened rapidly to prevent illegal import of alcohol via mislabelling. No other techniques can do the same job so easily and so fast (< 1 min). Because of differences in bottle diameters, glass colours, light absorptions or dispersion, and possible misalignment of bottles in the light path, SRS intensities must be normalized to a reference. A He-Ne laser beam may be passed coaxially with the pump laser beam through the bottle. It will be detected later on by the same PDA detector to produce a reference line in the SRS spectrum for normalization of the alcohol Stokes intensity.

SRS can also be used to screen various inorganic acids in their original bottles without sampling. The SRS spectra of glacial acetic acid (99.7% v/v), hydrochloric acid (37-38% v/v), nitric acid (70-71% v/v), phosphoric acid (40% v/v), and sulfuric acid

(95.5-96.5% v/v) were obtained by passing the laser light through their bottles which varied in diameter from 8 to 15 cm. As shown in Fig. 39, all of the examined acids were easily differentiated from one another by comparing and contrasting their SRS shifts. No SRS activity is expected from HCl which is completely ionized in water. A list of SRS shifts for inorganic acids is summarized in Table 4.

Table 4. SRS shifts of inorganic acids as measured in their original bottles.

Compound	Bottle Color	Bottle Diameter (cm)	SRS Shifts (cm ⁻¹)	Spectral Assignment
Acetic acid	clear	15	2964 2 x 2964 ^a	$\nu_1(\text{C-H})$
Hydrochloric acid	clear	15	NA ^b	
Nitric acid	clear	15	1312 2 x 1312	$\nu_1(\text{NO}_3)$
Phosphoric acid	amber	8	884.5	$\nu_1(\text{PO}_4)$
Sulfuric acid	clear	15	888 920 2 x 888	$\nu_1(\text{SO}_4)$

^a second-order Stokes shift is given as 2 x first-order Stokes shift.

^b NA = not SRS active.

Fig. 39. SRS spectra of inorganic acids, all contained in their original bottles.

4.11 Process Chemical Analysis

The application of analytical monitoring to the determination of components in industrial process streams has been under development for decades. Recent developments in fibre optics, sensor miniaturization and powerful microprocessor chips have combined to fuel increasing interest in process instrumentation among academic, government and industrial researchers [85]. The use of SRS on process chemical analysis and the arena of process control is a new idea. SRS is capable of discriminating between components of a mixture due to unique spectroscopic features pertaining to individual species [68]. Several parameters of the SRS radiation (i.e., scattering efficiency, frequency shift from the pump laser, and spectral band shape) all provide detailed information on the sample under examination. Since the SRS signal is related to an average analyte concentration integrated over the laser interaction length (minimum light path through the sample ≈ 2 cm), it better represents the bulk concentration of large-volume samples. By comparison, extended sample thicknesses beyond several centimetres are not readily afforded by spontaneous Raman or infrared absorption spectroscopy. The SRS instrumentation is not complex, requiring only a powerful pulsed laser to stimulate Raman scattering and a sensitive detector to capture the dispersed Stokes intensity.

Since a large proportion of the petrochemical industry is concerned either with the production of polymerizable monomers or with the reaction of these monomers to form polymers, in-situ monitoring of methylmethacrylate (MMA) polymerization was chosen to demonstrate the ability of SRS in process monitoring. In this section, we will also discuss the components and requirements of process SRS analyzers and explore

potential applications of SRS on batch reactors. Since flow velocity has no effect on the SRS intensity, the same principles will also apply to flowing liquid streams.

First, the ability of the SRS technique to obtain good-quality spectra quickly from monomer and polymer chemicals stored in amber-coloured bottles was again tested. The SRS spectrum of fresh styrene monomer in an amber-coloured bottle with a 15-cm diameter is shown in Fig. 40(a). This spectrum was obtained by placing the bottle instead of the sample cell in the laser beam path, using an accumulation of 125 spectra over 24 s. Unlike spontaneous Raman scattering, most substances show only one or two Stokes lines in the SRS spectrum. As a result, spectral interference is reduced to a minimum in the simultaneous determination of SRS-active components in a mixture. The band at 1629.6 cm^{-1} is due to the C=C stretching vibration of the exocyclic double bond through which polymerization occurs. In comparison, an old bottle (15-cm diameter) of styrene produced the spectrum shown in Fig. 40(b). As the Stokes intensity at 1629.6 cm^{-1} in the SRS spectrum amounted to 18% of that for fresh styrene, the styrene inside appeared to be a transparent block of solid polymer, the old styrene was indeed partially polymerized. After a close examination, it turned out that the chemical was not fully solid (i.e., polymerized) but rather gel-like. A completely polymerized solid bulk of polystyrene in its original bottle would record the spectrum shown in Fig 40(c). It is evident that the SRS peak due to the carbon double bond is totally gone. This investigation demonstrates what a powerful technique SRS is for the in-bottle analysis of chemicals in a short time of 24 s for each spectrum.

Second, the homopolymerization of MMA using 2,2'-azobis-isobutyronitrile (AIBN) as the initiator was studied in-situ as a model industrial reaction system inside

Fig. 40. SRS spectrum of (a) fresh styrene (b) partially polymerized styrene after 3 years of storage, and (c) polystyrene, all contained in an amber-colored bottle (15-cm in diameter).

a 10-cm-long jacketed cylindrical reactor. Fresh MMA monomer was treated with a small amount of AIBN (in a $\sim 200:1$ monomer/initiator weight ratio) [86]. The mixture was then allowed to polymerize at 40°C over 2 hr to give a transparent, glassy polymer. Generally, the simple optical configuration of a regular SRS setup means that any special cell designed for high or low temperatures and pressures can readily be accommodated in the spectrometer. This allows the polymerization to be studied under a wide range of conditions resembling those used at a large-scale chemical plant. The bulk homopolymerization of MMA can be followed by monitoring the disappearance of the SRS line centred at 2941.6 cm^{-1} , and experimental results are shown in Fig. 41. By keeping all of the spectroscopic conditions (e.g., laser energy, PDA integration time, etc.) constant and monitoring the change in the integrated area of the SRS peak, one can quantify the process of polymerization. The use of a multichannel PDA detector makes it possible to obtain a large number of consecutive spectra in a relatively short time. This enables reactions to be followed in time period ranging from a few minutes to several hours under simulated plant conditions (such as temperature, pressure, atmosphere, etc.). The time development of these SRS spectra can be compared favourably with the SRS spectra of MMA (Stokes shift = 2941.6 cm^{-1}) and partially polymerized MMA (Stokes shifts = 2940 and 2950 cm^{-1}) after 1.5 h displayed in Fig. 42(a) and 42(b), respectively. As it is shown, the structural changes during the course of polymerization reaction may also be investigated by analyzing the band shape. The fairly broad SRS band of the monomer resolved into two major peaks, showing different C-H vibrational modes at a high % conversion of the monomer to the polymer. The concentration threshold requirement renders the technique suitable for monitoring

Fig. 41 SRS spectra from in-situ monitoring of methylmethacrylate (MMA) polymerization at 40°C over 2 hr.

Fig. 42 SRS spectrum of (a) MMA monomer (Stokes shift = 2941.6 cm^{-1}), and (b) partially polymerized MMA. Stokes shift = 2945 and 2980 cm^{-1} .

analytes at relatively high concentrations, with little or no sensitivity to small amounts of other constituents (e.g., 0.5% AIBN) in the same sample.

In Fig. 43 the SRS spectrum of a mixture (1:4 ratio) of styrene in MMA is shown. The styrene SRS peak at 1629.6 cm^{-1} is far apart from that for MMA at 2941.6 cm^{-1} , which clearly indicates that the copolymerization of styrene and MMA can be studied by monitoring their SRS peaks independently. This represents an advantage over in-situ spontaneous Raman studies of the copolymerization, where the overlap of the vinyl groups of the two monomers (at 1640 cm^{-1}) is so severe that deconvolution was necessary to resolve them [87].

The collection optics for SRS can be remote from the sample and yet efficient in collecting the coherent SRS radiation. The PDA detector in our setup was located over 3 m away from the sample cell. The remote sensing geometry for SRS radiation collection can be readily adapted to hostile environments or difficult-to-reach sites where the close placement of optics next to the sample becomes impossible. The technique may also be applied to highly toxic, corrosive, or explosive chemical systems which must be isolated from the spectrometer and the operator. The remote SRS collection optics also becomes advantageous in situations where background luminescence from the sample is considerable.

A refractive index detector of the deflection type (designed in our laboratory) was also employed as an independent means for the simultaneous monitoring of MMA polymerization as shown in Fig. 44. A 0.5-mW probe beam from a He-Ne laser (Uniphase 1508 P-O, San Jose, California) was passed perpendicular to the SRS sample cell (diameter = 1.5 cm, cell length = 10 cm) and directed to a position

Fig. 43 SRS spectrum of a mixture of styrene in MMA (1:4 ratio).

Fig. 44 Experimental setup for monitoring of MMA polymerization at 40°C with both SRS and a refractive index detector.

sensitive detector (EG&G Photon Devices Division, model 1L10, Salem, Massachusetts). As the beam is deflected, corresponding to changes in refractive index due to sample polymerization, it will fall on a different spot on the position sensor and a new detector output signal will be recorded. Experimental results indicated that this simple technique was equally effective in following the polymerization to detect the end of the polymerization process. However, no spectral information is afforded by such refractive index detection to identify the changing nature of the chemical system. The traditional method for obtaining polymerization information is by dilatometry [88,89]. It is an indirect method that relates a physical property (volume contraction) to the extent of a chemical reaction. While this method has proved extremely successful from both a scientific and commercial point of view, it does have some specific limitations that the SRS technique does not have. For instance, dilatometry cannot be used to follow reactions to high levels of completion, and it is limited in the range of temperatures and pressures that can be employed. Dilatometry, also, does not have the capability of monitoring certain chemical systems under in-situ and real-time conditions. UV, IR, ESR and NMR spectroscopies are all useful for the structural investigation of polymers [90]. Except for UV absorption at 230 nm [91], these techniques are not promising for monitoring polymerization in batch reactors of large volumes. Therefore, the use of SRS promises to have a considerable impact on industrial polymerization studies.

The requirements for process SRS analyzers are quite different from those of laboratory SRS instruments. Considerations ranging from analyzer durability to hands-off continuous operation must be part of the design criteria. The introduction of small laser diodes presents new opportunities for monitoring process variables by SRS that are

not easily determined by other process analytical techniques. Some of the commercially available laser diodes have reduced or nearly eliminated the power dissipation and hence potential hazards in the chemical/industrial workplace, allowing the laser to be placed anywhere in the processing plant. Furthermore, these lasers may last for as long as 10 years which substantially lowers the long-term cost of the analyzer.

In conclusion, this work demonstrates for the first time that SRS is a useful semi-quantitative spectroscopic technique for the non-invasive, in-situ, real-time monitoring of chemical processes such as the polymerization reactions considered above. The remote sensing capability of SRS is valuable in following both directly and non-invasively the chemistry as it occurs.

CHAPTER V

CONCLUSIONS

The development of SRS in this work has established the technique as a valuable spectroscopic tool for chemical analysis. The fundamental principles and useful applications of SRS to non-invasive, real-time chemical process monitoring have been fully discussed and demonstrated. The spectral characteristics of over two hundred organic compounds have established SRS as a versatile technique for the detection and quantification of organic substances. Recent developments of the SRS technique for use in analytical chemistry have been motivated by the great demand in controlling industrial processes where non-invasive, real-time measurements on chemical components are essential. Our work has aimed towards increasing both the detection sensitivity and selectivity of the technique. Various approaches such as IASRS, low temperature, large interaction volume, and sensitive photomultiplier detector can enhance sensitivity and improve detection limits significantly. The technique is useful for the quantitative determination of organic compounds at the hundreds of part-per-million or higher level. The focused beam configuration is appropriate whenever a low laser energy (or power) is desired or a short cell length is encountered. In addition, it can be used to measure the concentration distribution of an analyte in a large-volume sample.

The concentration threshold used to present a major obstacle in the improvement of detection limits in SRS spectroscopic analysis [3]. It has been proven to be caused by a lack of sufficient Stokes photons for stimulation of excited molecules to produce

amplification of the Stokes wave. It is now possible to determine the analyte at concentration levels below its SRS threshold by using an appropriate amplifier compound at constant concentration in the sample solution. A numerical analysis of the spectral overlap between the analyte and amplifier SRS peaks, as well as their changes in FWHM, versus amplification coefficient (k') has showed that k' is maximized when the analyte and amplifier completely overlap.

SRS may be used to advantage in the measurement of high analyte concentrations. At the relatively high concentrations where SRS is best utilized, the stimulated Stokes intensity may be comparable to that of the pump laser while the spontaneous Raman lines are down by several orders of magnitude [68]. Under these analytical conditions, the Stokes intensity can be easily detected by a PMT equipped with appropriate interference band-pass filters and HNFs (to extinguish the laser line). No expensive, big monochromator would be required to complicate the instrumentation. Extension of the linear dynamic range of the SRS technique is achieved through the use of an optimum pump laser intensity and cell length in order to avoid signal saturation. As the analytical sensitivity of SRS measurements increases exponentially with increasing analyte concentration (up to the point of saturation), the higher the analyte concentration, the more sensitive the technique is to small changes in analyte concentration. This unique characteristic of SRS could be valuable in situations where the exact concentration of a major constituent in the chemical system must be determined.

The more exciting possibilities, however, are found in the potential applications of SRS in probing dynamic processes in the chemical industry. A model industrial chemical system, the polymerization of methyl methacrylate in bulk, has been

successfully monitored. As the technique is noninvasive and does not require sampling, separations or other pretreatment procedures, and with the increased emphasis on moving chemical instrumentation next to the chemical process, SRS is a promising technique for adaptation to industrial monitoring. SRS can develop to be a versatile instrument that is easily optimized for a number of applications using the same basic optical configuration (including a single laser source or λ_p) and changing only few operating parameters. The lack of sensitivity to changes in flow velocity and sample cell position (relative to the focusing lens) may be regarded as two additional advantages in process monitoring applications.

Although SRS is not yet a familiar technique in the industrial laboratory, it will likely become an important technique for process monitoring as further advances in instrumentation are made over the next several years. Since the intensity of SRS is related to an average analyte concentration integrated over the laser interaction length (on the order of 5-50 cm), it can better represent the bulk property of large-volume samples. Thus, the SRS technique is particularly useful where extended sample thicknesses beyond 1 mm are not readily afforded by the complementary method of infrared spectroscopy. For those samples with dimensions greater than 50 cm, an advantage of SRS over spontaneous Raman spectroscopy would be the much simpler optics for the collection of coherent Stokes radiation. Indeed, the remote sensing geometry for SRS collection can readily be adapted to hostile environments or difficult-to-reach sites where the close placement of optics next to the sample becomes impossible. SRS is particularly attractive in aqueous-system studies that are beyond the reach of infrared absorption spectroscopy.

CLAIMS TO ORIGINAL RESEARCH

Our objective has been to develop an SRS spectrometer for non-invasive, real-time monitoring of chemicals in industrial processes and hazardous effluent streams. The main goal is to attain direct identification and simultaneous determination of organic compounds without sampling, separations or other pretreatment procedures. The newly-examined SRS activities of over one hundred organic compounds have been compiled to supplement a previous list of known SRS-active compounds [68]. The overall results show that SRS activity is a universal property among organic liquids. Different theoretical and experimental aspects of SRS have been examined and evaluated to make the analytical technique more sensitive. Specifically, our study has confirmed that greater Stokes intensity and hence higher sensitivity can be obtained at lower sample temperature [28]. A novel approach, internally amplified stimulated Raman scattering (IASRS), has been developed to lower concentration thresholds, leading to improved detection limits [44]. Results show that there are no significant changes in the Stokes intensity when the sample flow velocity is varied from 0 to 6 m s⁻¹. This characteristic is promising for fast-flowing process monitoring applications. This work demonstrates for the first time that SRS is a useful spectroscopic technique for the non-invasive, in-situ, real-time monitoring of chemical processes such as polymerization reactions. The technique is applicable to the screening of high and low alcohol contents in white wines and of different acids in their original bottles.

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APPENDIX I

SRS APPLICATIONS

A.1 Tunable Radiation

The SRS of dye laser radiation in H_2 gas provides a convenient method to produce widely-tunable radiation in the infrared spectral region. With a near-IR dye laser system pumped by a giga-watt ruby laser, Frey et al generated tunable IR radiation up to $7.7 \mu m$ with two consecutive Stokes processes in H_2 [92]. The SRS in H_2 , D_2 , and CH_4 using mode-locked pulses of approximately 100-ps duration at 1.06 and $0.53 \mu m$ in two different pumping geometries (tight focusing and waveguiding in hollow capillary) could provide a convenient source of tunable short pulses in the near-infrared [32]. A laser rangefinder emitting at an eye-safe wavelength of $1.54 \mu m$ was designed. It was a Raman-shifted laser where a Nd-YAG laser emitting at a wavelength of $1.06 \mu m$ was used to pump a Raman cell containing CH_4 gas at a very high pressure, resulting in the Stokes radiation at $1.54 \mu m$. Conversion efficiencies were as high as 40% and continued efforts were on to increase them close to the theoretical limits [93].

Efficient Raman shifting of ultraviolet excimer laser radiation has received considerable attention in the past several years as a means of generating high-power coherent radiation in the near ultraviolet and the visible region especially in the blue-green region. Experimental demonstration of high conversion efficiencies was reported for various atomic media (e.g. lead and barium vapor) using a relatively short ultraviolet pump pulse with low laser energies [94]. Lou et al measured the energy of the Stokes

emission as a function of incident laser energy at constant lead pressure. The experimental curve showed that saturation occurred at high pump input energy. Lai and Harris recently utilized the second harmonic 532-nm output from a Nd-YAG laser to generate SRS emission from a neat organic compound contained in a Raman shifter [63]. The Stokes radiation was combined with the residual pump beam, and together they were focused into a sample cell to induce stimulated Raman gain spectroscopy (SRGS) of the same organic compound at low concentrations. In this way, the spatial and temporal overlap of the two pulsed laser beams in the sample was guaranteed. Since the frequency difference between the pump and the Stokes radiations always matched the molecular vibrational frequency of the analyte compound, there was strong coupling between the light waves and the mechanical waves of coherently driven molecular vibrations during the nonlinear SRGS process. This approach greatly simplified the SRGS instrumentation as no second laser was needed to provide the Stokes radiation.

The propagation of relatively long and powerful pulses over moderate lengths of single-mode fiber could give rise to the highly efficient generation of new wavelengths by SRS with an associated depletion of the pump. For silica-based fibers the peak of the Raman gain was observed for shifts near 400 cm^{-1} [95,96]. Optical amplification due to SRS in an 800-m-long single-mode silica optical fiber doped with 17 mol% P_2O_5 was achieved [97]. With the combination of a $1.32\text{-}\mu\text{m}$ pump and a $1.59\text{-}\mu\text{m}$ signal, a net power gain of 15.4 dB at the wavelength of $1.59\text{ }\mu\text{m}$ was obtained for a pump power of 15 W, and the optical power ratio of the amplified signal to the spontaneous emission was about 25 dB at the first Stokes line. The mechanism of competition and transformation between SRS and stimulated four-photon mixing was analyzed [98]. Six

pairs of Stokes and anti-Stokes lines in a multimode fiber with a $\text{GeO}_3 + \text{P}_2\text{O}_5$ doped silica core were simultaneously recorded. A continuum band generated jointly by SRS and stimulated four-photon mixing was obtained in the spectral range 540-640 nm for 20 m and 200 m of fiber.

A.2 Micrometer-size Liquid Droplets

Pioneering experiments on SRS in micrometer-size liquid droplets (diameters from 20 to 180 μm) were conducted at Yale by Chang and coworkers [98,100]. The droplets acted as lenses and focused the incident beam. The droplets could also sustain standing surface modes which enhanced the signal where the circumference was equal to an integral number of wavelengths of the Stokes scattered light. The loss was significantly lowered, leading to much lower thresholds for oscillation than in bulk. The result was a series of regularly spaced peaks known as morphology-dependent resonances (MDRs), whose separation was governed by the droplet diameter. Recently, the threshold behavior of SRS from binary liquid mixture micrometer-sized droplets (14-16 μm radius) has been reported [101]. Droplet SRS thresholds were determined by component concentrations and refractive indices. The threshold for SRS was greatly reduced if the liquid was in the form of an aerosol.

Conventional SRS experiments were carried out in long samples and the high value of interaction length z lead to suppression of all but the main peak which had reached threshold. In droplets, z was much smaller than in bulk experiments and, consequently, the damping of other molecular peaks was small. The existence of spatial modes in the droplet allowed lower-gain parts of the spontaneous bulk spectrum to

oscillate first. The SRS in these droplets gave information on molecular composition from a number of subsidiary molecular peaks which were related to maxima observed in the spontaneous Raman cross-section [62]. SRS emissions at Stokes shifts corresponding to combination frequencies of the individual component Stokes shifts were also observed in droplets but not in bulk mixtures [101]. Strong SRS could occur at multiorder or combination Stokes lines when there was an MDR near each of the combination lines [102]. This contrasted with the bulk liquid where only one peak was observed. Such a phenomenon can have wide applications in the study of evaporation and pre-combustion processes in engine fuel droplets.

Although the pumping region in the droplet was confined to the narrow entry and exit focal spots of the incident laser beam, the SRS from the droplet was nearly isotropic. The angular scattering characteristics and time-resolved profiles have been measured successfully for SRS in micrometer-sized droplets of water, ethanol and CCl_4 [103,104]. Based on the intensity dependence of the time profiles, it was deduced that the photon lifetime within a droplet is limited by the depletion of the internal intensity in generating nonlinear-optical radiation [105]. Furthermore, the electromagnetic field enhancement in the forward direction of a small dielectric sphere (or liquid droplet) was derived using geometric optics. The theory predicted the enhancement near the droplet surface, producing high energy density in an inner critical ring region where the SRS process was experimentally observed. Effective enhancement of the fields in 120- μm spherical water droplets was demonstrated. The SRS radiation continued to be confined to the well defined ring on water droplets as small as 50 μm in diameter [106].

APPENDIX II

FORMERLY REPORTED SRS SHIFTS AND GAIN FACTORS OF VARIOUS MATERIALS

Table 5: Formerly reported SRS shifts and gain factors of various materials¹.

Compound	SRS shift (cm ⁻¹)	Gain factor (cm W ⁻¹)
I ₂	211	
LiTaO ₃ (80 K)	215	1×10^{-8}
	608	7.9×10^{-9}
(300 K)	201	4.4×10^{-9}
	600	4.3×10^{-9}
α -Sulfur	216	
	472	
	946	
LiNbO ₃ (80 K)	258	2.9×10^{-8}
	643	1.3×10^{-8}
(300 K)	256	1.8×10^{-8}
	637	9.4×10^{-9}
InSb	300	
Quartz	420	1.7×10^{-11}
Tetrachloroethylene, C ₂ Cl ₄	446.9	1.7×10^{-9}
Carbon tetrachloride	460.6	1.3×10^{-9}
	2x460.6	
	1393	
	2569.44	
SiO ₂	467	8×10^{-10}
Methylene bromide	580	
Ba ₂ NaNb ₅ O ₁₅ (80 K)	655	1.9×10^{-8}
(300 K)	650	6.7×10^{-9}
Carbon disulfide	656.5	1×10^{-8}
Ethylene bromide	660	
Chloroform	667	

(continued)

Table 5 (continued)

Compound	SRS shift (cm ⁻¹)	Gain factor (cm W ⁻¹)
KGd(WO ₄) ₂ :Nd ³⁺	899.3	
KY(WO ₄) ₂ :Nd ³⁺	901.5	
Calcium tungstate	911	
Deuterated benzene	944.3 2 x 944 2292	
Benzene	992 2 x 992 3064	5 x 10 ⁻⁹
1,3-Dibromobenzene	992	
Pyridine	992 2 x 992 3054	
Aniline	997	
Styrene	999 1315 1631 3056	
Bromobenzene	1000	1.5 x 10 ⁻⁹
t-Butylbenzene	1000	
Benzaldehyde	1001	
Benzonitrile	1002 2229	
Chlorobenzene	1002	1.9 x 10 ⁻⁹

(continued)

Table 5 (continued)

Compound	SRS shift (cm ⁻¹)	Gain factor (cm W ⁻¹)
Ethyl Benzene	1002 3051-3117	
Toluene	1004 3078.5	1.2 x 10 ⁻⁹
Fluorobenzene	1009	
1-Fluoro-2-chlorobenzene	1034	
Calcite	1075 2171	5.5 x 10 ⁻⁹
Diamond	1325	6.9 x 10 ⁻⁹
Nitrobenzene	1344 2 x 1346 3 x 1340 2661	2.1 x 10 ⁻⁹
1-Bromonaphthalene	1368 3060	
1-Chloronaphthalene	1368	
2-Ethyl naphthalene	1382	
Carbon dioxide	1388	7 x 10 ⁻¹⁰
Oxygen (liquid)	1552	1.6 x 10 ⁻⁸
Oxygen (90 K)	1552	14.5 x 10 ⁻⁹
Cinnamaldehyde	1624	
3-Methyl-1,3-butadiene	1638	
1,3-Pentadiene	1655	
1-Hexyne	2116 2915	

(continued)

Table 5 (continued)

Compound	SRS shift (cm ⁻¹)	Gain factor (cm W ⁻¹)
Carbon monoxide	2143	7 x 10 ⁻¹⁰
Nitrogen (liquid at 77 K) (gas)	2326.5	1.8 x 10 ⁻⁸ 3.5 x 10 ⁻¹¹
D ₂ O 23°C 62°C	2385-2405 2485-2495	
Methanol	2837	4 x 10 ⁻¹⁰
1,3-Dimethylcyclohexane	2844	
Tetrahydrofuran	2849 2939	
Cyclohexane	2852 801 3656.09	
cis 1,2-Dimethyl- cyclohexane	2853 2921	
Cyclohexanone	2863 2945	
Heptane	2870	
cis 1,4-Dimethyl- cyclohexane	2876	
Pentane	2876	
Isopropyl alcohol	2882	9.2 x 10 ⁻¹⁰
Propylene oxide, C ₃ H ₆ O	2882.5	
2,3-Dimethyl-1,5-hexadiene	2910	
Dimethyl sulfide	2910	

(continued)

Table 5 (continued)

Compound	SRS shift (cm ⁻¹)	Gain factor (cm W ⁻¹)
o-Xylene	2913	
	2922	
	2933	
	730	
cis 2-Heptene	2915	
Methane	2916	6.3 x 10 ⁻⁹
2-Octene	2918	
2-Bromopropane	2920	
Acetone	2921	1.2 x 10 ⁻⁹
2-Chloro-2-methylbutane	2927	
Ethanol	2928	5.1 x 10 ⁻⁹
Ethylene glycol, (CH ₂ OH) ₂	2932	
Piperidine	2933	
	2936	
	2940	
	2943	
m-Xylene	2933	
1,2-Diethylbenzene	2934	
1-Bromopropane	2935	
	2962	
1,1,1-Trichloroethane	2939	5.1 x 10 ⁻⁹
2-Nitropropane	2945	
1,1,2,2-Tetrachloroethane	2984	

(continued)

Table 5 (continued)

Compound	SRS shift (cm ⁻¹)	Gain factor (cm W ⁻¹)
Dichloromethane	2985.54 697.88	
Deuterium (gas) (different stimulated lines appear at differ- ent temperatures and laser polarizations)	2991 2992.1 2996.4 414 170	
p-Xylene	2998	$\leq 10^{-9}$
Dichloroethane	3011.98 728.46	
Water 23°C 62°C	3380-3410 3405-3415	1×10^{-10}
60% H ₂ O - 40% D ₂ O 50% H ₂ O - 50% D ₂ O	3415 3425 2475-2510	
4 M NaClO ₄ in H ₂ O	3450	
Hydrogen (77 K and 300 K)	4155	1.5×10^{-9}
Anthracene (crystals)	1400	
o-Dichlorobenzene	NA ²	
Lead (vapor)	10681	$\leq 10^{-9}$

(1) Original references for all the compounds listed can be found in Reference 3.

(2) NA = not SRS active.

END

1 8-0 7-9 4

FIN