

Development of Femtosecond Stimulated Raman Spectroscopy: Stimulated Raman Gain via Elimination of Cross Phase Modulation

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Received September 6, 2004

We have developed a new femtosecond probe technique by using stimulated Raman spectroscopy. The cross phase modulation in femtosecond time scale associated with off-resonant interaction was shown to be eliminated by integrating the transient gain/loss signal over the time delay between the Raman pump pulse and the continuum pulse. The stimulated Raman gain of neat cyclohexane was obtained to demonstrate the feasibility of the technique. Spectral and temporal widths of stimulated Raman spectra were controlled by using a narrow band pass filter. Femtosecond stimulated Raman spectroscopy was proposed as a highly useful probe in time-resolved vibrational spectroscopy.

Key Words : Stimulated Raman, Raman gain, Cross phase modulation, Femtochemistry

Introduction

Since Zewail and coworkers applied femtosecond time-resolved spectroscopy to observe real time photolysis reactions of small molecules in the 1980s,^{1,2} femtochemistry has made a great progress in the field of molecular reaction dynamics. Femtochemistry has been applied to unravel reaction mechanisms of numerous photochemical reactions in the gas phase by using ionization,^{1,2} fluorescence,^{3,4} and photoelectron⁵ spectroscopies. In the condensed phase, on the other hand, other techniques have been developed to address chemical processes in real time, including transient absorption and transient hole burning to probe ultrafast dynamics of electronic and vibrational excited states. A major drawback of transient absorption is, however, its typically broad electronic absorption spectra that come short of giving sufficient information for analyzing changes in chemical bonds and molecular geometry during a photochemical reaction.

One of the methods that directly observe changes in chemical bonds is impulsive stimulated Raman spectroscopy (ISRS).⁶⁻¹⁰ Since a laser pulse shorter than vibrational period of molecules has been developed, the spectral and dynamical ranges of ISRS have been expanded to cover many chemical systems. In ISRS, a short pulse excites vibrational modes coherently, and the change in its amplitude or phase is observed as an oscillating decay signal, whose Fourier transformation yields vibrational frequencies as well as their dephasing time. This method has been used to obtain information on relaxation and reorganization of solvents and solutes. However, ISRS is not specific to the vibrational mode of interest and its temporal resolution is several vibrational periods or longer.⁶

Time-resolved coherent anti-Stokes Raman scattering (CARS) has been a widely used technique for monitoring

vibrational frequency changes in femtosecond time scale.¹¹ Although CARS is linked with homodyne detection and shows high sensitivity, the phase-matching condition dictates that the direction of its signal beam varies constantly as the Raman frequency changes.¹² Therefore it is difficult to obtain a dispersed Raman spectrum in a fixed optical configuration.

In the picosecond regime, time-resolved resonance Raman spectroscopy has elucidated many photochemical reaction mechanisms.¹³⁻¹⁷ The low sensitivity of conventional Raman scattering is overcome by resonance effect, which enhances a Raman signal by 10⁶-10⁸ times. Time-resolved resonance Raman spectroscopy tends to suffer, however, from complications such as interference with spontaneous fluorescence that most molecules are capable of emitting in the excited state.

To overcome many of these shortcomings, several research groups attempted to improve the sensitivity of Raman spectroscopy in the 1970s by developing CW and nanosecond stimulated Raman spectroscopy (SRS) in combination with optical heterodyne detection.¹⁸⁻²⁰

The stimulated Raman gain (SRG) represents one of the third-order nonlinear optical processes.^{12,20,21} Through the temporal and spatial interaction of the Raman pump pulse (ω_{RP}) and the Stokes-shifted continuum pulse (ω_c), photon creation can occur at frequencies resonant with vibrational energy gap. The SRG can be defined as^{12,19-21}

$$I_c(z) = I_c(0) \exp(Gz) \quad (1)$$

$$G \propto \text{Im}[\chi_{SRG}^{(3)}(\omega_c)] I_{RP} \propto (\partial^2 \sigma / \partial \omega \partial \Omega)_0 I_{RP}, \quad (2)$$

where G , z , I_{RP} and $(\partial^2 \sigma / \partial \omega \partial \Omega)_0$ are the SRG, the path length of the sample, the intensity of the Raman pump pulse, and the spontaneous Raman cross section, respectively. The fact that the SRG is proportional to the spontaneous Raman cross section means that the spectra obtained by SRS can be readily interpreted by comparing with the known spontaneous Raman spectra. The SRG signal is known to have a Lorentzian line shape due to the detection of only the

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imaginary part of the third-order susceptibility.²² A major benefit of SRS is the auto-phase matching condition, which allows one to monitor a wide spectral range without any change in optical configurations.²²⁻²⁷ In SRS, one can use a near IR Raman pump to avoid various resonance effects such as resonance Raman scattering and stimulated emission from the excited state as well as the wavepacket dynamics¹⁴ on the excited state.

The SRG can be obtained experimentally by using

$$G = \frac{1}{z} \ln [I_c(z)/I_c(0)]. \quad (3)$$

Recently, Mathies *et al.*²²⁻²⁵ and Yoshizawa *et al.*^{26,27} observed time-resolved Raman spectra using SRS. They improved spectral resolution by inserting a narrow band pass filter (NBPF) into the Raman pump without doing time-integration over the time delay between the Raman pump pulse and the continuum pulse. When femtosecond pulses are involved, however, as in the case of Mathies *et al.* and Yoshizawa *et al.*'s work, coherent artifacts such as the cross phase modulation (XPM) can occur,²⁸ and therefore, a procedure that extracts and discards such coherent artifacts has to be taken in order to observe genuine stimulated Raman signal.

The present paper describes the method of eliminating XPM from transient gain/loss signals to obtain a genuine femtosecond SRG, which carries vibrational information with no coherent artifact for a molecular system, whether stationary or undergoing a chemical transformation.

Experimental Section

Figure 1 shows a schematic diagram of our femtosecond SRS setup. A femtosecond pulse (130 fs, 120 cm⁻¹, 650 μJ, 1 kHz) centered at 800 nm was generated by a typical regenerative-amplified Ti: Sapphire laser (Hurricane, Spectra Physics). The pulse was split into a Raman pump pulse and a continuum pulse. The continuum light was generated by focusing the 800-nm light by a planoconvex lens ($f = 10$ cm) into a flowing water cell (RD250, Lambda Physik), which proved to be a superior medium for continuum generation to fused silica or sapphire. The Raman pump light had a diameter of ~150 μm ($f = 50$ cm) and the continuum light~100 μm ($f = 35$ cm). The continuum pulse covered a sufficiently wide spectral range for vibrational spectroscopy down to 1110 nm, *i.e.*, ~3500 cm⁻¹ of Raman frequency shift. The continuum light was divided into a signal pulse and a reference pulse using a broadband beamsplitter (BBS-650-1100-1025-45, CVI). To prevent chirping of the continuum light, gold-coated metal mirrors and concave mirrors were used.

Once the 800-nm Raman pulse pumps the molecule to a virtual state, the continuum pulse stimulates the Raman emission, producing a SRG at Raman frequencies of the molecule. The polarization angle of the Raman pump pulse was controlled using a zero-order half-waveplate for 800 nm (QWPO-800-06-2-R, CVI). The polarizations of the Raman

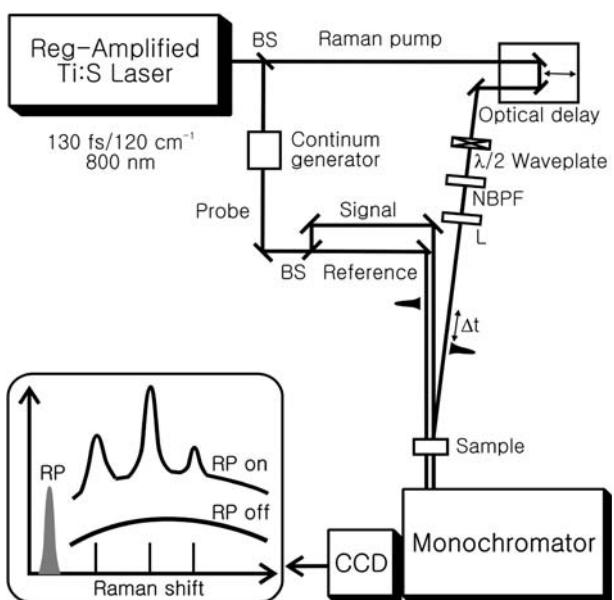


Figure 1. Schematic diagram of the experimental setup for femtosecond SRS. L, plano-convex lens; BS, beam splitter; NBPF, narrow band pass filter; RP, Raman pump.

pump pulse and the continuum pulse were parallel to each other. For better spectral resolution, the Raman pump light was allowed to pass through a narrow band pass filter (NBPF: F1.5-800-4-1.00, CVI). The full-width-half-maximum (FWHM) of the filter was 1.7 nm (26.5 cm⁻¹). The optical time delay between the Raman pump pulse and the continuum pulse was scanned by a delay stage (ODL-150, Clark-MXR) and the time range was set to cover all time-dependent gain and loss signal. The pulse energy of the Raman pump light was 2 μJ/pulse.

The continuum and Raman pump pulses were focused into a flowing liquid cell (DLC-S25, Harrick) containing the sample. Cyclohexane (HPLC grade, Aldrich) was purchased and used without further purification. The optical path length of the sample cell was 0.5 mm. A magnetic drive gear pump (G184, Micropump) delivers the solution at a flow rate of 160 mL/min. The probe pulse of the signal and reference lights was detected by CCD (SpectraMM 256F, 256 × 1064, Acton Research Corp.) after dispersing the continuum light using a monochromator (250is/sm, grating of 600 grooves blazed at 750 nm, Chromex). The intensity of the signal and reference lights was normalized to reduce the power fluctuation of the laser. At a fixed grating position of 890 nm, the spectral range of the CCD detector was 840 to 960 nm, which corresponds to a Raman frequency of 590 to 2100 cm⁻¹. The spectral resolution was ~0.12 nm (~1.5 cm⁻¹), which was much narrower than the bandwidth of the Raman pump light (130 cm⁻¹ without NBPF, 27 cm⁻¹ with NBPF).

The signal intensity (I_s) and the reference intensity (I_r) of the continuum light were measured by controlling the region-of-interest (ROI) pixels of the CCD detector. The signal intensity was divided by the reference intensity, which significantly removed shot-to-shot fluctuation of the continuum pulse itself. The normalized signal (I_s/I_r) depends

on the time delay (t_d) between the Raman pump pulse and the continuum pulse. It was divided by another normalized signal measured at a blank position ($t_d \ll 0$, the continuum light preceding the Raman pump light) to yield the transient gain/loss $D(t_d)$, which we define as

$$D(t_d) \equiv \ln \{ [(I_s/I_r)(t = t_d)] / [(I_s/I_r)(t \ll 0)]_{\text{blank}} \} . \quad (4)$$

In order to eliminate the XPM due to coherent artifact, the transient gain/loss $D(t_d)$ was integrated

$$G = \int D(t_d) dt_d , \quad (5)$$

where the time integration was carried out until no gain/loss was observed. An SRG spectrum was obtained through the signal processing procedure described above.

Results and Discussion

Figure 2(a) shows a 3-D plot of the transient gain/loss signal for neat cyclohexane as functions of the Raman frequency shift as well as the time delay. The transient gain/loss signal in both the Raman active and Raman inactive regions (respectively denoted (1) and (2) in Figure 2(a)) shows a coherent ringing spike around time zero (Fig. 2(b)). The transient gain/loss signal in the Raman active region consists of the SRG as well as the XPM, whereas the coherent spike in the Raman inactive region reflects only a coherent artifact that has no relation to an actual vibrational transition. The origin of the coherent artifact is of purely electronic nature.²⁸⁻³⁰ Temporal overlap of two or more pulses often generates transient gain/loss signals even in off-resonance case, which does not include one- or two-photon absorption or Raman resonance. The transient gain/loss signal results from the XPM through some sort of a laser-induced change in the refractive index. Since the XPM results from instantaneous electronic response, it carries no vibrational information for the molecule.²⁹ It is almost impossible to predict how the amplitude and phase of the XPM would change as a function of the Raman frequency in real system. Therefore, it is crucial to eliminate the XPM entirely from the transient gain/loss signal.

Since the electronic gain/loss (g_e)²⁹ is a real function, the time-integrated signal at any continuum wavelength must be zero, that is, there is no net absorption in nonresonant case:

$$\int dt_d g_e \approx \text{Im } g_e = 0 . \quad (6)$$

Therefore, the *time-integrated* Raman gain should reflect a pure vibrational spectrum, totally free from coherent artifacts of electronic origin. The time delay of a given peak depends on the wavelength, which means that the phase change of the refractive index is not constant along the wavelength. In accord with Ernsting *et al.*'s suggestion²⁹ for the time integration of the transient gain/loss signal due to the fluctuating amplitude of the XPM, we propose that the signal should be completely integrated over the time delay covering the entire transient signal in the spectral regions of interest in order to exclusively discard the effect of the XPM

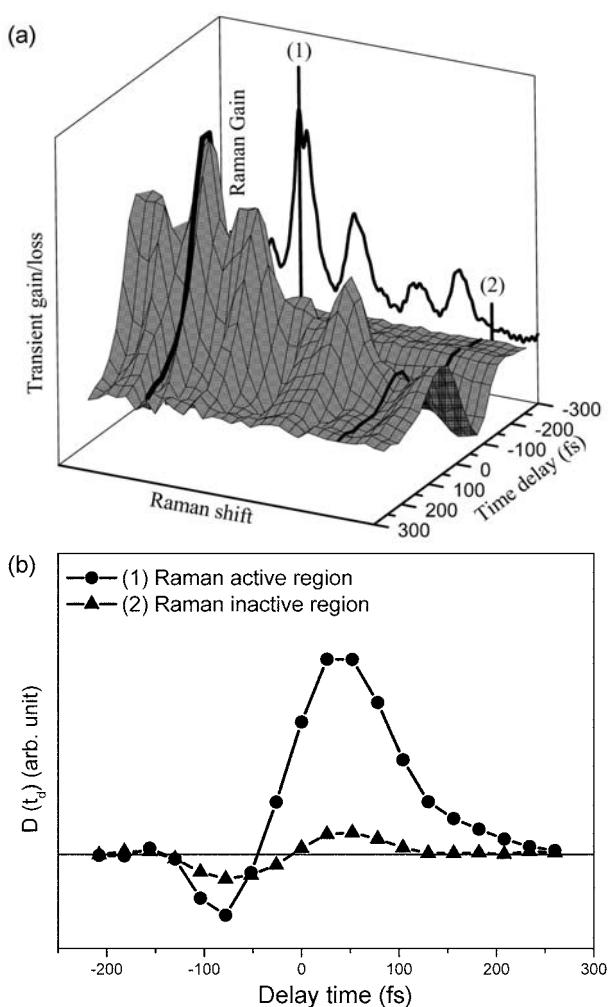


Figure 2. (a) 3-D spectrum for the transient gain/loss signal of neat cyclohexane as functions of the Raman frequency shift and the time delay between the Raman pump and the continuum pulse. The time for maximum gain varies along the Raman frequency due to the XPM. The signal in the Raman active region (1) has a compound contribution from the XPM as well as from genuine vibrational transition, whereas the signal in the Raman inactive region (2) has a contribution from the XPM only. (b) Transient gain/loss signal of neat cyclohexane as a function of the above time delay. The signal from the Raman inactive region due entirely to the XPM averages out to zero, while that from the Raman active region yields a pure vibrational SRG upon time integration.

from the transient gain/loss signal.

An NBPF inserted into the Raman pump light path enhances spectral resolution of SRS.^{22,26} Figure 3(b) shows highly improved spectral resolution over that of Figure 3(a) obtained without NBPF. It should be noted that, with or without NBPF, the time-bandwidth-product of the Raman pump pulse is in near Fourier transform limit. The spectral resolution is easily controlled by just inserting a proper NBPF into the Raman pump light path. Of course, the enhancement in the spectral resolution does not violate the uncertainty principle, since better spectral resolution comes with worse temporal resolution. Without any filter inserted, the transient gain/loss signal was integrated for 500 fs over the time delay, while we had to integrate it for ~1 ps with an

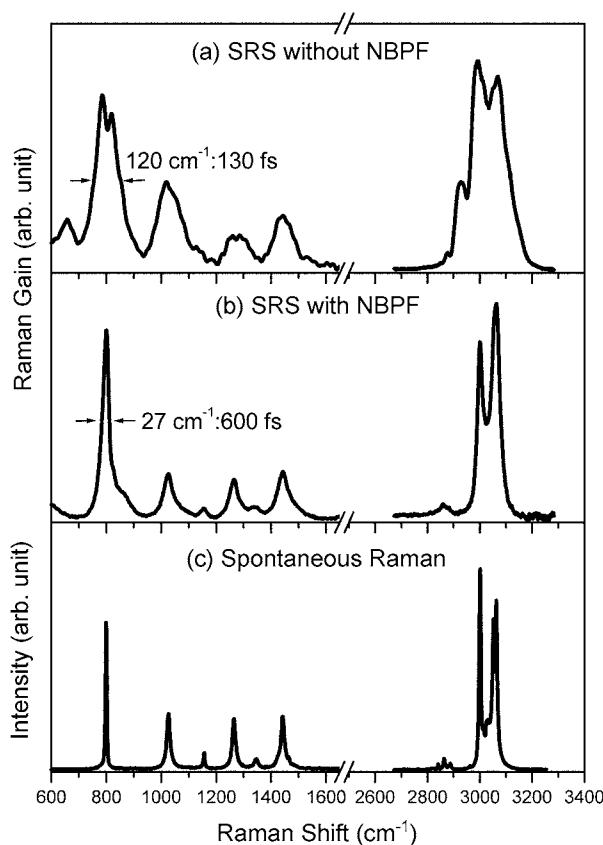


Figure 3. Time-integrated SRS spectra of neat cyclohexane obtained (a) without any filter and (b) with NBPF. (c) Raman spectrum obtained by the conventional Raman scattering method with a CW Ar ion laser. The Raman activity in 600–700 cm⁻¹ in (a) and (b) comes from cell windows (fused silica).

NBPF of $\sim 27 \text{ cm}^{-1}$ spectral resolution. The integration time was determined to cover all transient gain/loss signals. A variety of spectral resolutions were available just by inserting a filter with appropriate bandwidth into the path of the Raman pump light.

We suggest that the present technique of femtosecond SRS can be used as a real-time probe in a typical femtosecond pump-probe experiment to temporally track a given chemical process.

Conclusion

We have succeeded in developing a new femtosecond time-resolved vibrational spectroscopic method. Two femtosecond pulses of what we call the Raman pump and continuum light interact nonlinear-optically to result in a stimulated Raman gain or loss signal. To eliminate the XPM, the transient gain/loss was integrated over the entire time delay, which yielded a pure vibrational stimulated Raman

spectrum with femtosecond time resolution. To achieve better spectral resolution at the expense of temporal resolution, we inserted an NBPF into the path of the Raman pump light. With a third femtosecond pulse to initiate a given chemical process, femtosecond SRS can be turned into transient stimulated Raman spectroscopy.

Acknowledgements. This work was supported by the French-Korean International Co-operation Program of KOSEF (F01-2003-000-00111-0) and also by KOSEF-CRM.

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