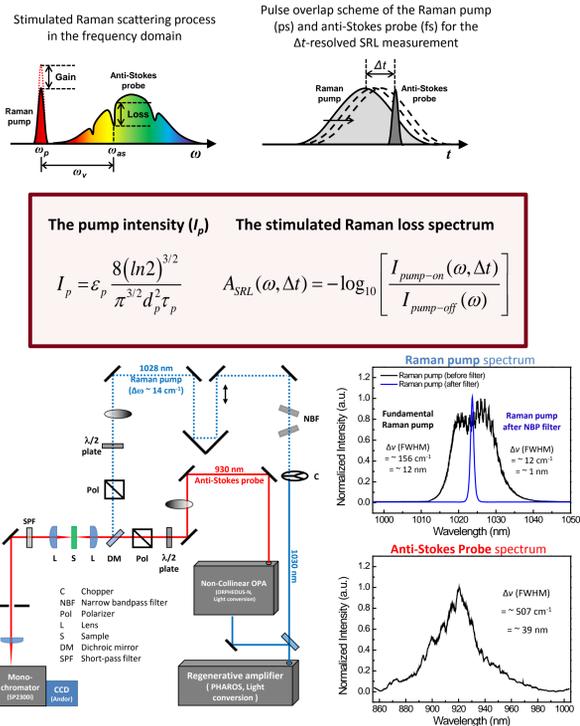


Introduction

Raman spectroscopy provides valuable information on molecular vibrations and has been widely used to investigate chemical structure of molecule. Nevertheless, due to the notoriously small cross sections of spontaneous Raman scatterings, conventional Raman technique often suffers from the weak spontaneous Raman signal, which has limited more in-depth applications. Stimulated Raman scattering (SRS) spectroscopy is an advanced Raman technique that involves a coherent multiphoton interaction making a significant Raman enhancement.

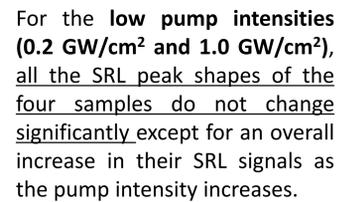
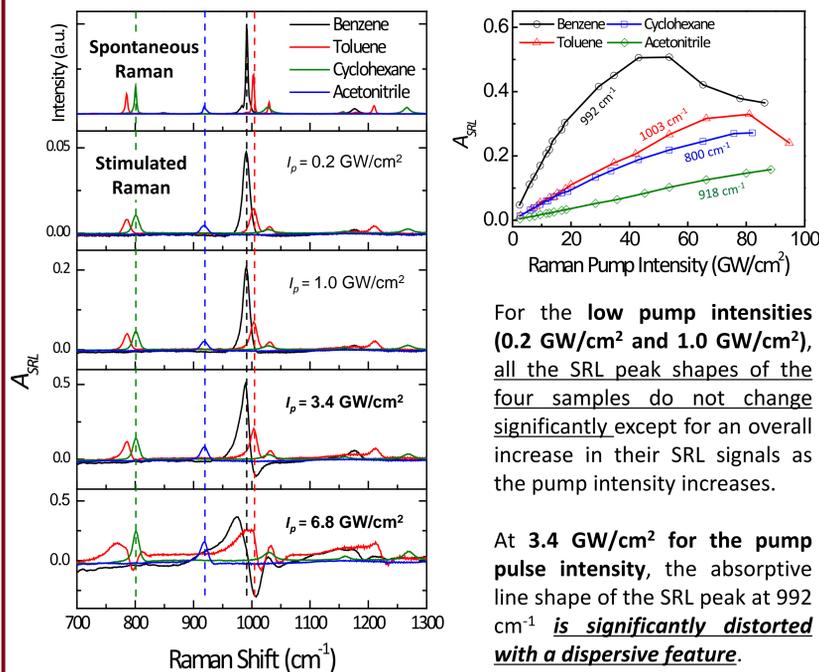
In this work, we perform an intensity-dependent SRL spectroscopy for several organic solvents with variable Raman pump intensity. Aromatic (more polarizable) and non-aromatic (less polarizable) molecules with large and small optical Kerr non-linearity, respectively, are considered to examine the dependence of their SRL spectra on the pump intensity. To account for the distorted spectral shape of the SRL at the high pump intensity, we performed numerical simulation using a split-step Fourier algorithm to calculate the SRL spectra including both the vibrationally resonant Raman susceptibility and non-resonant XPM and compare the numerical simulation and experimental results. In our narrowband picosecond (ps) pump-broadband femtosecond (fs) probe SRL measurement, a scan of the time delay (Δt) between the pump and probe pulses allows one to monitor an overall time- and frequency-resolved modulation in SRS. To investigate the pump-probe delay time dependence of the XPM effect, the measured and calculated time-resolved SRL spectra at the high and low pump intensities are also compared.

Experimental Methods



Results and Discussions Pump intensity dependence of SRL spectrum

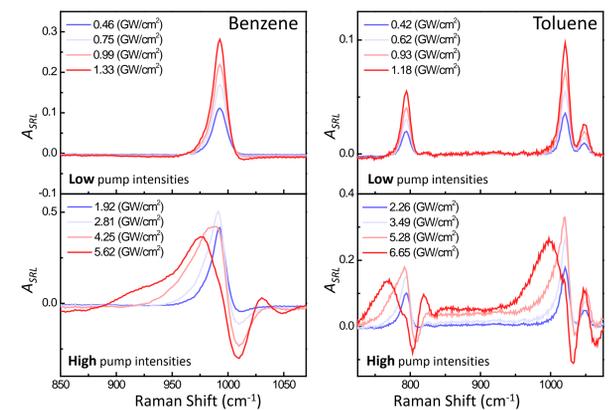
The SRL spectra of benzene, toluene, cyclohexane, and acetonitrile measured at $\Delta t_{max} = 0$



For the low pump intensities (0.2 GW/cm² and 1.0 GW/cm²), all the SRL peak shapes of the four samples do not change significantly except for an overall increase in their SRL signals as the pump intensity increases.

At 3.4 GW/cm² for the pump pulse intensity, the absorptive line shape of the SRL peak at 992 cm⁻¹ is significantly distorted with a dispersive feature.

Spectral modulation of the stimulated Raman loss



The SRL spectral shapes of the aromatic compounds are significantly modified from the original ones at the high pump intensity.

These nonlinear increasing pattern and spectral distortion of the SRL signal upon increasing pump intensity imply that other nonlinear optical effects such as XPM should be properly taken into account because they start to interfere with the SRS process at high pump intensities.

Numerical Simulation Methods

The Maxwell equation for the electric field

$$\frac{\partial^2 E(z,t)}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 E(z,t)}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2}{\partial t^2} \{P_L(z,t) + P_{NL}(z,t)\}$$

The total electric field (E)

$$E(z,t) = E_p(z,t + \Delta t) + E_{as}(z,t)$$

$$= A_p(z,t + \Delta t) \exp[i(k_p z - \omega_p(t + \Delta t))] + A_{as}(z,t) \exp[i(k_{as} z - \omega_{as} t)] + c.c.$$

The initial amplitudes of the pump and probe pulses at z=0

$$A_p(z=0, t + \Delta t) = A_p^0 \exp[-2 \ln(2) \cdot (t + \Delta t)^2 / \tau_p^2] \quad \text{Raman pump}$$

$$A_{as}(z=0, t) = A_{as}^0 \exp[-2 \ln(2) \cdot t^2 / \tau_{as}^2] \quad \text{Anti-Stokes probe}$$

Applying the slowly varying envelope approximation in time and space, the wave propagation equation can be written as

$$\frac{\partial A_p}{\partial z} + \left(\beta_p^{(1)} \frac{\partial A_p}{\partial t} + \frac{i}{2} \beta_p^{(2)} \frac{\partial^2 A_p}{\partial t^2} \right) \approx \frac{i\omega_p}{2c} n_2 |A_p|^2 A_p, \quad \text{Raman pump}$$

$$\frac{\partial A_{as}}{\partial z} + \left(\beta_{as}^{(1)} \frac{\partial A_{as}}{\partial t} + \frac{i}{2} \beta_{as}^{(2)} \frac{\partial^2 A_{as}}{\partial t^2} \right) \approx \frac{i\omega_{as}}{2c} n_2 |A_p(z,t + \Delta t)|^2 A_{as}(z,t) + \frac{2\pi\omega_{as}}{n_0 c} P_R^{(3)}(z,t) e^{-i(k_{as} z - \omega_{as} t)}$$

$$\approx \frac{i\omega_{as}}{c} n_2 |A_p(z,t + \Delta t)|^2 A_{as}(z,t) + \frac{2\pi\omega_{as}}{n_0 c} P_R^{(3)}(z,t) e^{-i(k_{as} z - \omega_{as} t)}$$

$$\approx \frac{i\omega_{as}}{c} n_2 |A_p(z,t + \Delta t)|^2 A_{as}(z,t) + \frac{2\pi\omega_{as}}{n_0 c} P_R^{(3)}(z,t) e^{-i(k_{as} z - \omega_{as} t)}$$

$$\text{where } n_2 = \frac{6\pi}{n_0} \chi_{NR}^{(3)}(-\omega_{as}; \omega_p, \omega_p, -\omega_p)$$

The Fourier transform of third-order polarizability

$$FT[P_R^{(3)}(z,t)] = P_R^{(3)}(z,\omega) = \chi_R^{(3)}(\omega, \Delta t) |A_p^0|^2 E_{as}^{pump-off}(z,\omega)$$

Using the split-step Fourier algorithm,

$$\text{Time field } A_{as}(t) \xrightarrow{\text{Fourier-transform}} \text{Spectral field } A_{as}(\omega)$$

$$A_{as}(dz,t) = A_{as}(0,t) \exp(i d\phi_{as})$$

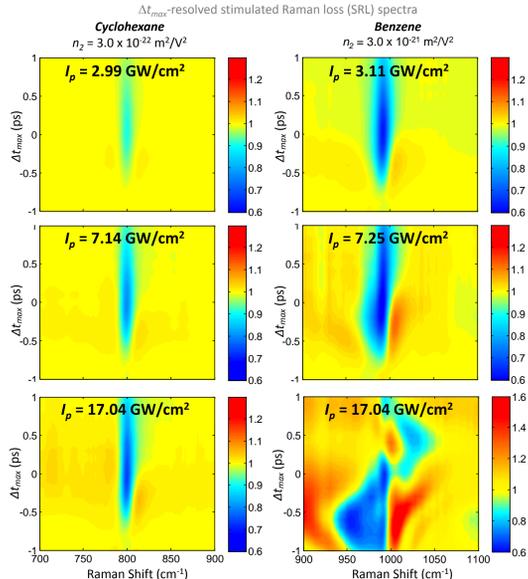
$$d\phi_{as} = n_2 \omega_{as} |A_p(0,t + \Delta t)|^2 dz / c$$

$$A_{as}(dz,\omega) = A_{as}(\omega) h(dz,\omega)$$

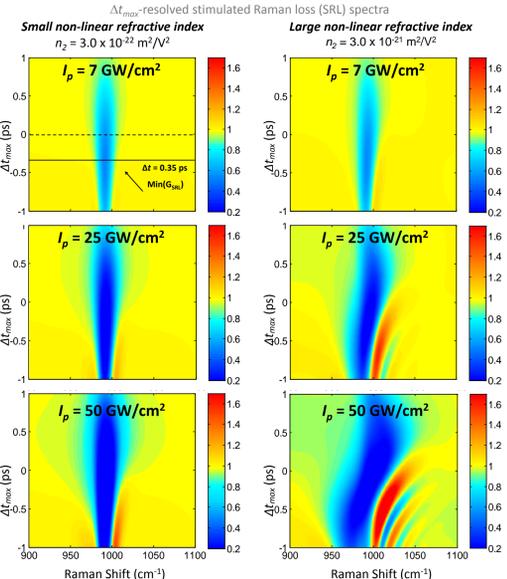
$$h(dz,\omega) = \exp \left[i \frac{2\pi\omega_{as}}{n_0 c} \chi_R^{(3)}(\omega) |A_p^0|^2 dz \right]$$

Results and Discussions Pump-probe delay time-dependence of SRL spectrum

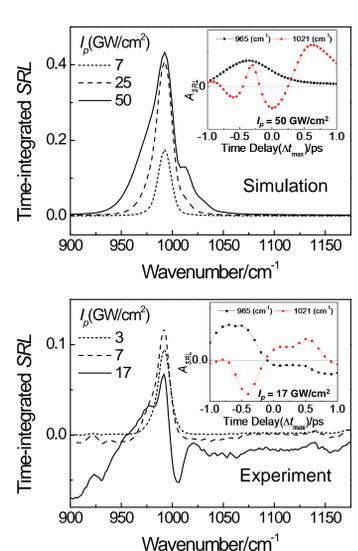
Experimentally measured



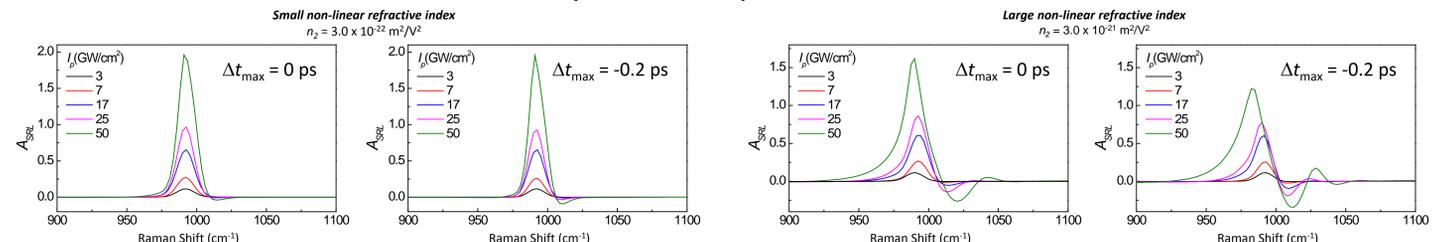
Numerically simulated



Time-integrated stimulated Raman loss (SRL) spectra



Numerically simulated SRL spectra of the model cases



Conclusions

- One should be careful in choosing a proper set of experimental parameters, such as probe frequency and bandwidth. Without prior information on the entire spectral characteristics, any inappropriate choice of them could give rise to quantitatively undesired results (even sign of the loss signal could be reversed).
- The SRL spectra taken at positive delay times are less contaminated by the strongly modulated interference signal. Therefore, SRS measurement at a slightly positive time delay could be more favorable for obtaining a better SRS signal.
- Molecules with aromatic rings (large n_2) might be less suitable as imaging probe for super-resolution SRS imaging because the undesired XPM effect is large and the SRS signal is more vulnerable to the intense pump beam. Through this study, the unusual spectroscopic features in SRS observed beyond the weak Raman pump limit and their possible origin have been elucidated. We anticipate that our results will provide useful information for SRS application employing an extremely intense pump beam, for example, super-resolution SRS imaging.