

Enhanced and broadened SRS spectra of toluene mixed with chloroform in liquid-core fiber

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Abstract: Stimulated Raman scattering of toluene and its mixture with chloroform is studied in liquid-core optical fiber. The results show a remarkably broadened Raman line of the mixture from about 630nm to 650nm by a pumping wavelength at 532nm, which is assigned to the interaction of CH vibrations of the two liquids. The results suggest that interactions between adjacent vibrations can produce strong and wide Raman spectra in liquid-core fiber which may prove a new simple way for supercontinuum generation.

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Introduction

Liquid-core fiber was first investigated by Bell Lab in 1970 [1], and immediately caught tense attention. Thanks to the unique advantages of liquids such as high nonlinear and tunable property, this kind of fiber has been extensively studied. All of the research results prove that the fiber can be well applied in a wide range of optical fields including spectroscopy, sensor and supercontinuum generation [2–12]. For its usage in spectroscopy, stimulated scatterings such as Stimulated Kerr scattering (SKS) and Stimulated Raman scattering (SRS) of liquids grab the most attention [2–8]. Because of the small interaction area and long interaction length, significantly strong and remarkable SRS spectra are produced in fiber which provides wide applications in nonlinear optics like laser modeling, supercontinuum generation, infrared or ultraviolet light generation and so on [13–16]. As Raman spectroscopy offers a direct approach to study the structures and interactions of molecules, it should also become a powerful method to investigate solvent/solute interactions in liquid-core fiber.

In this paper, we studied the SRS spectra of liquid mixtures in liquid-core fiber, which to our knowledge, have been seldom reported. Two important liquids toluene and chloroform were chosen as our sample because their refractive index is higher or lower than the silica cladding which makes the refractive index of the liquid core tunable. Moreover they both have the CH vibrations at adjacent energy levels, which has not been paid much attention to in the earlier research [6]. We aim to get some visible information of the interactions between these molecular vibrations. Owing to the intense SRS process in fiber, the Stokes of the CH stretching mode (3060cm^{-1}) of toluene in addition to Stokes of the aromatic ring (1006cm^{-1}) have been successfully observed when stimulated by Nd:YAG laser. We still found some exciting phenomena, including obviously broadened SRS spectra of toluene when mixed with chloroform during the experiment, which indicates the effects of vibrations interaction and may find potential applications in nonlinear optics such as a new approach for supercontinuum generation.

Experiment

The experimental setup is illustrated in Fig. 1. The pump is Nd:YAG laser which delivers light pulses with pulse width of 50ps, repetition frequency of 10Hz and a center wavelength of 532nm. A $10\times$ object lens was used to focus the light into the end of the liquid-core fiber, and an optical spectrometer was adopted to detect the SRS spectra immediately after the exit end of the fiber. The average power of our input light before the focus lens can be tuned from 40mw to 80mw and the spectra we studied below were obtained from an average power around 60mw.

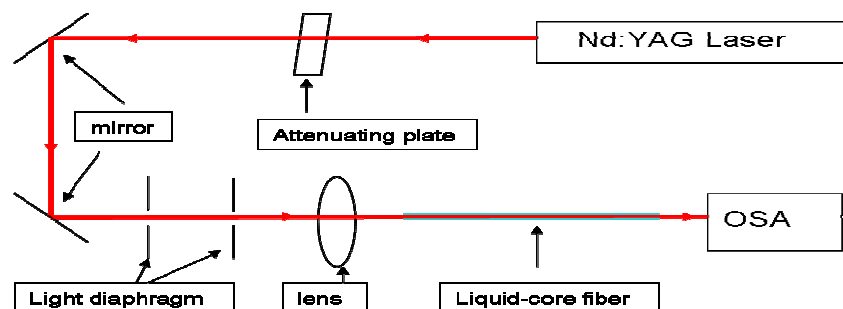


Fig. 1. Experimental setup.

The liquid-core fiber in the experiment is made from hollow silica fibers that are commercially obtained from Polymicro Technologies with an outer diameter of $360\mu\text{m}$ and an inner diameter of $50\mu\text{m}$. The fiber is first stripped of its protection layer and cut smoothly at its end, then fixed into two quartz glass tubes. Quartz glasses with thickness of 1mm are adhibited onto the end of tubes acting as the entrance and exit window of fiber. One of the tubes is filled with the liquid at the beginning and lifted higher, so the liquid is leaded into the hollow core by capillary actions and gravity force spontaneously, after that the other tube is also filled with liquid to make the liquid-core fiber stable. The length of fiber in our experiment is 22cm and the transmission of it in our experiment is approximately 35% . It should be noted that there is a slight variation of the transmission efficiency of the liquid-core fiber. This unstableness limits us from exactly quantitative analysis of the results, but the general analysis of the results, however, is unaffected.

Results and analysis

Mixtures of toluene and chloroform with different mixing ratios as well as neat toluene were studied. Since the refractive index of toluene (1.50) and chloroform (1.449) at 532nm and room temperature are larger or smaller than the silica cladding (1.461) respectively [17], the refractive index of the mixture will decrease with lower toluene concentration thus weaker liquid-core fiber's confinement of light. When light was coupled into the fiber, a bright central pattern was observed from the end of it surrounded by a similar weaker spotty, showing a complicated interference among propagation modes in the far field. Experimental results show that, the pump wavelength (532nm) is shifted mainly in 1006cm^{-1} steps of the aromatic ring to 562 , 596 , 634 , 677nm , and 3060cm^{-1} step of CH stretching mode to 636nm which is well accord with the standard SRS spectrum of toluene. The main vibration of chloroform at 667cm^{-1} steps were never observed in our experiment, which can be explained by the much smaller scattering cross section of chloroform compared with toluene [18,19].

We observed a general phenomenon that the SRS spectra of the mixture not only reveals the vibrational feature of toluene mainly but also are stronger than that of neat toluene as is shown in Fig. 2(a) and Fig. 3(a). Further more, some new peaks appear in the output spectra of the mixture. This dramatic change of SRS spectra in liquid-core fiber must find its value in molecular science, for instance, in the study of the properties of liquid modes and intermolecular interactions [20,21].

An exciting optical phenomenon we find from Fig. 2 (a) is an asymmetric broadened band from about 630nm to 650nm in the mixture which delighted us a lot. To understand the origin of this band, we adopt the curve fitting method to fit the line that turns out to be well fitted by five peaks as is shown in Fig. 2 (b). The peaks of different experimental lines vary a little but all around 634 , 636 , 641 and 645nm . By theoretical calculation, we find that the third-order Stokes of aromatic ring (1006cm^{-1}) and first-order stokes of CH-stretch of chloroform (3018cm^{-1}) stimulated by the pump light (532nm) are located at 634nm , yet the CH-SRS of toluene (3060cm^{-1}) is at 636nm . The peaks around 641nm and 645nm can be attributed to the co-effect of the CH-bend of toluene (1210cm^{-1}) and chloroform (1216cm^{-1}) stimulated by the

second-order Stokes of aromatic ring (596nm). These adjacent vibrational modes should resonate with each other and form a wide band of Raman gain in the mixture. We assume the main mechanism of it to be the Fermi resonance that will result in intensity borrowing between vibrational modes [22]. Effects of these resonances are further enhanced by the strong light interaction in fiber, which help produce the strong SRS line and the wide band from 630nm to 650nm. However resonances between vibrational modes are perturbation-sensitive, which results in slight shifts of SRS lines. This broadening effect instantly enlightens us that it can be applied in supercontinuum generation.

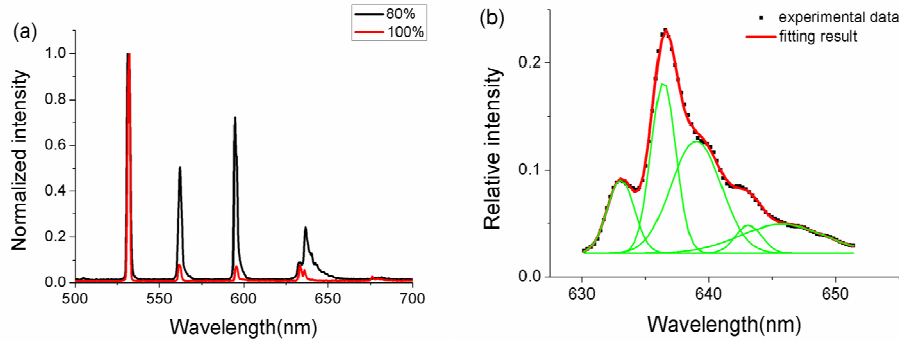


Fig. 2. (a) SRS spectra of the mixture with concentration of toluene at 80% and 100%. (b) Fitting result of the broadened band around 636nm.

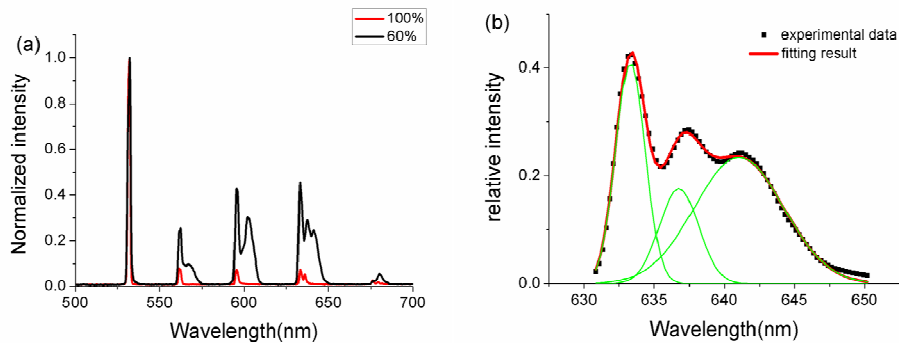


Fig. 3. (a) SRS spectra of the mixture with concentration of toluene at 60% and 100%. (b) fitting result of the broadened band around 636nm.

The most inspired spectrum for supercontinuum generation we got is from a mixture with 60% toluene as is shown in Fig. 3 (a). The spectrum shows not only SRS of aromatic ring (1006cm^{-1}) and CH-stretch (3060cm^{-1} , 3018cm^{-1}) but also CH-bend (1210cm^{-1} , 1216cm^{-1}) are efficiently stimulated at about 568, 603 and 642nm. These three new peaks are from the CH-bend (1210cm^{-1} , 1216cm^{-1}) line pumped by the pump light (532nm), first Stokes of 1006cm^{-1} line (562nm) and second Stokes of 1006cm^{-1} line (596nm) respectively. Resonances between the adjacent vibrations like CH-bend and CH-stretch enhance their scatterings and form these lines. The superposition of them results in broadened SRS bands as is pictured in Fig. 3 (a). The widest band from about 630nm to 650nm comprises three main peaks around 633, 637 and 641nm which are ascribed to the SRS of aromatic ring, CH-stretch and CH-bend respectively as is illustrated in Fig. 3 (b). Illumined by the property of this spectrum, we believe that if there are more resonant vibration-modes in the sample, scatterings of these modes should all be enhanced and super-positioned in the output SRS

spectrum to form a super-broadened band. For instance, if methylene chloride which has vibrations at 1148, 1417, 2985 and 304cm^{-1} [23] is contained in the sample, the second band (600nm) and third band (636nm) in Fig. 3 (a) can be even wider and vibration of toluene at 2918cm^{-1} may also be enhanced to stimulate Stokes light around 630nm, which can possibly connect two broadened bands at 600nm and 636nm. Moreover, when an appropriate longer liquid-core fiber is simultaneously adopted, these effects can be further enhanced and result in a stronger spectrum.

The broadened band of the spectrum can even be changed to another wavelength by using liquids with different typical vibrations, which offers a simple way for supercontinuum generation at selective wavelength. If a special-designed photonic bandgap fiber is used instead of conventional hollow fiber, the output spectra can also be limited to some given bands [8]. All of these phenomena are of optimistic applications in nonlinear optics.

Conclusion

To sum up, obviously broadened Raman spectra of toluene when mixed with chloroform were observed in liquid-core fiber during our experiment. The broadened band in the spectra can be assigned to resonances of CH vibrations that enhance their scatterings and form a wide band of Raman gain. The liquid-core fiber, moreover, helps to reinforce the SRS process further to produce strong output spectra. And we believe this broadened band can get much wider with more adjacent vibrations' interactions in the sample or in longer fibers and it can be produced at some specifically selected wavelength when appropriate liquids are used. Moreover, the wide band can also be selected in the output spectrum by using liquid-core PCF. This phenomenon should pave a new simple way for the supercontinuum generation and find its potential application in intermolecular science. The underlying mechanism of intermolecular interactions between toluene and chloroform in our experiment, however, needs further studying.

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