

Enhanced stimulated Raman scattering by intermolecular Fermi resonance

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Abstract We demonstrate the stimulated Raman scattering (SRS) of a binary solution of toluene and m-xylene at different volume concentrations in liquid-core optical fiber (LCOF). The results show that SRS of three vibration modes of 1002 cm^{-1} , 2920 cm^{-1} and 3058 cm^{-1} bands are simultaneously generated at some volume concentrations. The 2920 cm^{-1} band and the 3058 cm^{-1} band are generated at one time, the SRS thresholds of the first-order Stokes of the 2920 cm^{-1} and 3058 cm^{-1} bands are lower compared with the second-order Stokes threshold of the 1002 cm^{-1} band and the main peak of the 2920 cm^{-1} and 3058 cm^{-1} bands changes from the 2920 cm^{-1} band to the 3058 cm^{-1} band as the volume concentrations are changed. We assume that these phenomena are attributed to the intermolecular Fermi resonance. Raman scattering cross section (RSCS) theory is used to explain this assumption.

1 Introduction

Stimulated Raman scattering (SRS) has been an effective way to obtain multi-wavelength coherent light sources. It has applications in the areas of nonlinear optics, plasmas,

Raman lasers and Raman amplifiers [1–6]. However, the relevant application and research are limited because of the high SRS threshold and low SRS intensity. In order to lower the threshold of SRS and enhance the intensity of SRS, some methods are applied, such as fluorescent dyes to enhance the SRS [7], micrometer-sized droplets to enhance the SRS [8, 9], liquid-core optical fibers (LCOFs) to enhance the SRS [10], intramolecular Fermi resonance to enhance the SRS [11] and so on. The fluorescent dye enhancement to SRS in a LCOF has been investigated by our team in the last few years [12, 13]. But the intermolecular Fermi resonance to enhance the SRS has not been researched as far as we know.

Intermolecular Fermi resonance requires a close match of the vibrational energy levels and an appropriate dependence of the intermolecular potential on the normal coordinates for the two vibrational modes, and the intermolecular Fermi resonance can involve coupling between fundamental vibrations on two different molecules [14]. Because of the small interaction area and long interaction length, significantly strong and remarkable SRS spectra are produced in a LCOF, which provide wide applications in nonlinear optics such as laser modeling, supercontinuum generation and infrared or ultraviolet light generation [15–18]. The intensities of the spontaneous Raman scattering and the resonant Raman scattering were enhanced by 2–3 orders of magnitude by a LCOF [19, 20]. Meanwhile, the SRS threshold was drastically reduced.

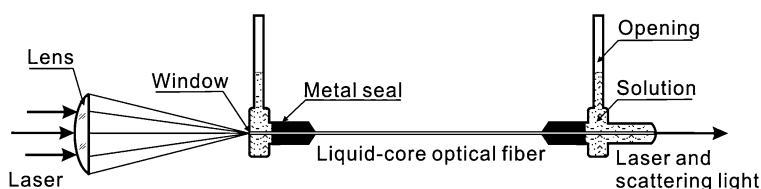
In this paper, we study the SRS of a binary solution of toluene and m-xylene in a LCOF. Firstly, toluene and m-xylene have CH vibrations at adjacent energy levels. Secondly, the refractive index of the binary solution is higher than the silica which is used to make the hollow-core optical fiber. We obtain three vibration modes that are simultaneously stimulated: the Stokes of the aromatic ring breathing

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Fig. 1 Schematic diagram of coupling between laser beam and LCOF



mode (1002 cm^{-1}), the Stokes of the CH-symmetric stretching vibration mode of $-\text{CH}_3$ (2920 cm^{-1}) and the Stokes of the CH-symmetric stretching vibration mode of the aromatic ring (3058 cm^{-1}), at different volume concentrations, respectively. We also find some exciting phenomena, including that the main peaks of the 2920 cm^{-1} and 3058 cm^{-1} bands are different at different volume concentrations, and the thresholds of the 2920 cm^{-1} and 3058 cm^{-1} bands are also changed. We assume that the intermolecular Fermi resonance results in these phenomena being generated. According to the SRS spectra, spontaneous Raman spectra and Raman scattering cross section (RSCS) theoretical calculation, the assumption is certified as correct.

2 Experiment

LCOFs of 80-cm length (inner diameter $400\text{ }\mu\text{m}$, outer diameter $600\text{ }\mu\text{m}$) are filled with different volume ratio binary solutions of toluene mixed with m-xylene (the volume concentrations of toluene are 0% (neat m-xylene), 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90% and 100% (neat toluene), respectively. The refractive indexes of the binary solution are 1.4927, 1.4957, 1.4954, 1.4950, 1.4947, 1.4944, 1.4940, 1.4937, 1.4938, 1.4930 and 1.4961, respectively. The LCOF is a highly multimode fiber. The facture of the LCOF is shown by previous papers [19–21]. The experimental setup is shown elsewhere [13].

A micro-Raman spectrometer (Renishaw InVia Raman microscope) is equipped with a 514.5-nm Ar^+ ion excitation laser (Spectra Physics 163-M42). A $20\times$ objective (LEICA DMLM 0.12NA) is used for both laser illumination and Raman backscattering detection.

As the excitation laser, a frequency-doubled Nd:YAG laser is used which emitted a laser pulse of duration 10 ns with a wavelength of 532 nm. It has a repetition rate of 1 Hz and a pulse energy in the range of 0–5 mJ. The laser is coupled to the core by a $25\times$ objective lens, the output light from the fiber is focused on the spectrometer and the signals are managed by a computer. For keeping a certain coupling efficiency and incident angle between the laser beam and the LCOF, we retain the end face of LCOF on the lens focus (Fig. 1), and the beam diameter at the focus is less than $400\text{ }\mu\text{m}$, so the pump power coupled into the LCOF is the same, and the same transverse mode is always in this condition.

The first- and second-order Stokes of the 1002 cm^{-1} band and the first-order Stokes of the 2920 cm^{-1} and 3058 cm^{-1} bands are measured, simultaneously, and the relationship of the thresholds of the 2920 cm^{-1} and 3058 cm^{-1} bands with their RSCSs is analyzed.

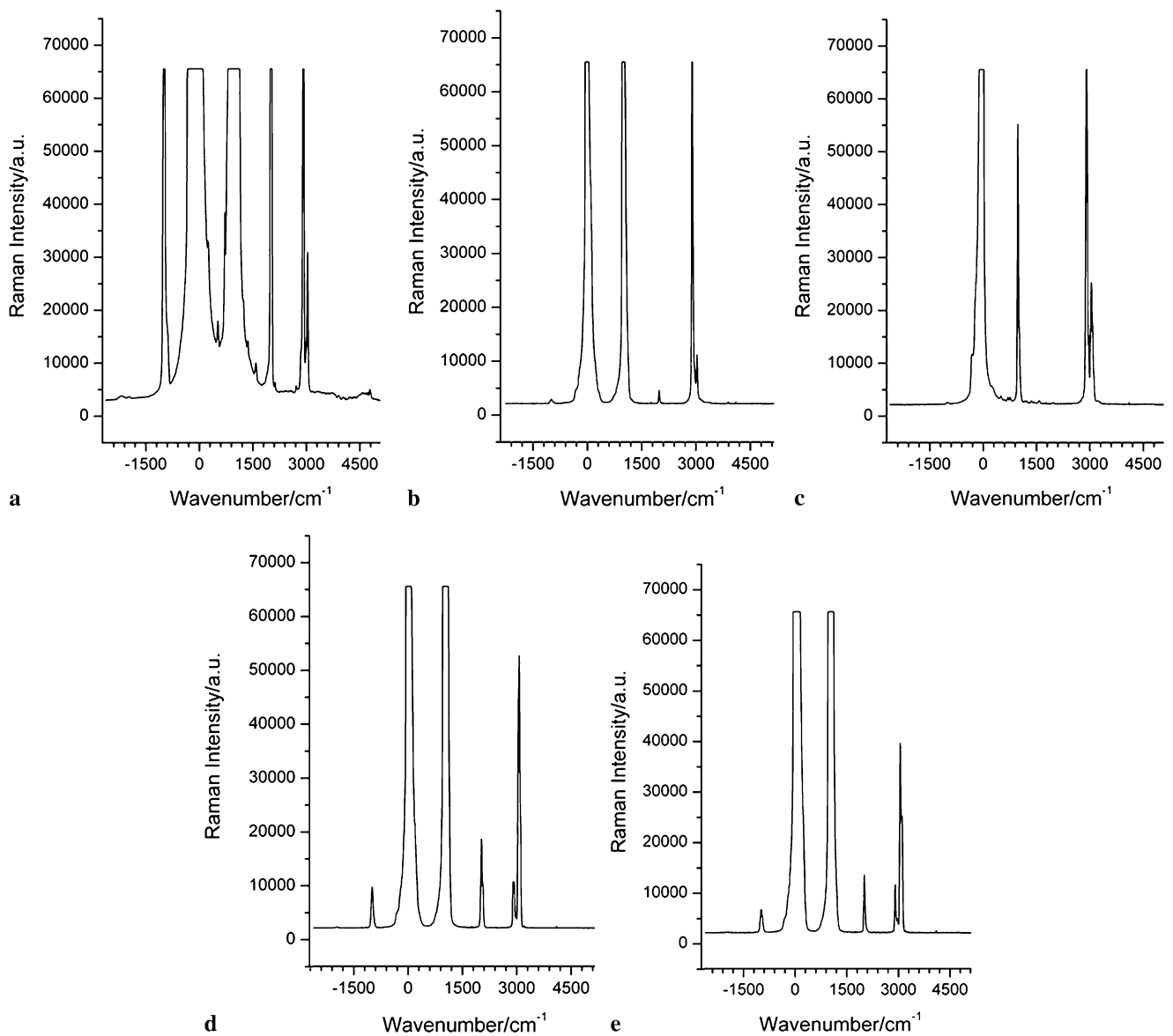
3 Results and discussion

The binary solutions of toluene and m-xylene at different volume concentrations in LCOFs were studied. Experimental results show that neat toluene and neat m-xylene both can generate the first- or second-order stimulated Raman Stokes of the 1002 cm^{-1} band at any volume concentration, but stimulated Raman Stokes of the 2920 cm^{-1} and 3058 cm^{-1} bands cannot be generated when the volume concentrations of toluene are 90%, 80%, 20% and 10%. When the volume concentrations of toluene are from 30% to 70%, some exciting phenomena can be obtained, as are shown in Fig. 2a, b, c, d and e. The Stokes of the 1002 cm^{-1} , 2920 cm^{-1} and 3058 cm^{-1} bands are stimulated, and the Stokes of the 2920 cm^{-1} and 3058 cm^{-1} bands are simultaneously stimulated all the time, but the first-order Stokes of the 1002 cm^{-1} band is earlier stimulated than the 2920 cm^{-1} and 3058 cm^{-1} bands. Table 1 shows the first- and second-order SRS thresholds of the 1002 cm^{-1} , 2920 cm^{-1} and 3058 cm^{-1} bands at different volume concentrations. In Fig. 2c, we find that only the first-order Stokes of the 1002 cm^{-1} band and the first-order Stokes of the 2920 cm^{-1} and 3058 cm^{-1} bands are stimulated; on the other hand, the first-order Stokes threshold of the 2920 cm^{-1} and 3058 cm^{-1} bands is much lower than the second-order Stokes of the 1002 cm^{-1} band. However, the first-order Stokes threshold of the 2920 cm^{-1} and 3058 cm^{-1} bands is always higher than the second-order Stokes threshold of the 1002 cm^{-1} band at other volume concentrations. Another exciting phenomenon is that the main stimulated Raman peak of the 2920 cm^{-1} band and the 3058 cm^{-1} band is different with varying volume concentrations. The main stimulated Raman peak is the 2920 cm^{-1} band, when volume concentrations of toluene are 30%, 40% and 50%, but the main stimulated Raman peak is the 3058 cm^{-1} band, when the volume concentrations of toluene are 60% and 70%.

We assume that the main mechanism of these phenomena can be attributed to the intermolecular Fermi resonance. The

Table 1 The SRS thresholds of a binary solution at different volume concentrations

$V_{\text{Tot}} : V_{\text{m-xy}}$	Stokes thresholds (mJ)		
	First order (1002 cm^{-1})	Second order (1002 cm^{-1})	First order (2920 cm^{-1} and 3058 cm^{-1})
1 : 9	1.12	1.68	
2 : 8	1.20	1.72	
3 : 7	1.42	2.04	2.76
4 : 6	2.76	3.80	4.28
5 : 5	2.56	4.28	2.76
6 : 4	1.42	2.04	2.76
7 : 3	1.35	1.96	2.68
8 : 2	1.21	1.80	
9 : 1	1.06	1.50	

**Fig. 2** SRS spectra of a binary solution of toluene and m-xylene with different volume concentrations in LCOFs. **a** 30%, **b** 40%, **c** 50%, **d** 60%, **e** 70%

spontaneous Raman scattering spectra of the binary solution of toluene mixed with m-xylene at different volume concentrations are shown in Fig. 3. Firstly, the 2920 cm⁻¹ band and the 3058 cm⁻¹ band belong to the CH-symmetric stretch of -CH₃ and the CH-symmetric stretch of the aromatic ring in the toluene or m-xylene, respectively. So, they have the same vibration mode. Secondly, intermolecular Fermi resonance can involve the interaction of fundamental vibrations on two different molecules. Thirdly, the spontaneous Raman spectrum of the 2920 cm⁻¹ and 3058 cm⁻¹ bands is broadened in the binary solution compared to the neat liquid. This broadening was confined to the CH-symmetric stretching vibration of -CH₃ (2920 cm⁻¹) and the CH-symmetric stretching vibration of the aromatic ring (3058 cm⁻¹), with the other modes of the binary solution not showing any such effect in going from the neat liquid to the solution state. We have used the RSCS to analyze these binary solutions in detail and have found that the 2920 cm⁻¹ and 3058 cm⁻¹ bands' dramatic increase is concentration dependent, Fig. 3, with the maximum increase corresponding to a 50% volume concentration. However, the positions of the bands' maxima were not found to be concentration dependent with the frequency shifting to higher or lower energies with dilution, because the 2920 cm⁻¹ band and the 3058 cm⁻¹ band are the same frequency in the toluene and the m-xylene, respectively. All observed data are consistent with the intermolecular Fermi resonance effect in which the RSCSs of the 2920 cm⁻¹ and 3058 cm⁻¹ bands are increased, observable by both peaks broadening [22]. The RSCS can be obtained according to the following equation [23] and the spontaneous Raman scattering spectra of Fig. 3.

$$\sigma_S = \sigma \cdot \left(\frac{I_S}{I_R} \right) \left[\frac{\nu_0(\nu_0 - \nu_R)^3}{\nu_0(\nu_0 - \nu_S)^3} \right] \left(\frac{C_R}{C_S} \right) \left(\frac{n^2 + 2}{3} \right)^4,$$

where σ is the RSCS of the 1002 cm⁻¹ band in the binary solution, the subscript S is the 2920 cm⁻¹ or 3058 cm⁻¹ Raman band of the binary solution and C_R and C_S are the molar concentrations of toluene and m-xylene, respectively. I_S/I_R is the spontaneous Raman intensity (peak areas) ratio of the 2920 cm⁻¹ or 3058 cm⁻¹ band to the 1002 cm⁻¹ band of toluene. ν_0 is the incident excitation beam wave number (cm⁻¹) and n is the refractive index of the binary solution.

The RSCS value of the 1002 cm⁻¹ band is a constant (1.83×10^{-29} cm² molecule⁻¹ Sr⁻¹) [24], but the 2920 cm⁻¹ and 3058 cm⁻¹ bands' RSCS values, as are shown in Table 2, change with varying volume concentrations. The RSCS value of the 1002 cm⁻¹ band is larger than that of the 2920 cm⁻¹ and 3058 cm⁻¹ bands when the volume concentrations of toluene are 90%, 80%, 20% and 10%. The Raman gain factor is [25]

$$g \approx \frac{\lambda^2}{\Delta S} \cdot N_a \cdot \sigma \cdot \frac{I(\nu_0) \cdot \lambda_0^2}{h\nu_0 \cdot \Delta\nu_0},$$

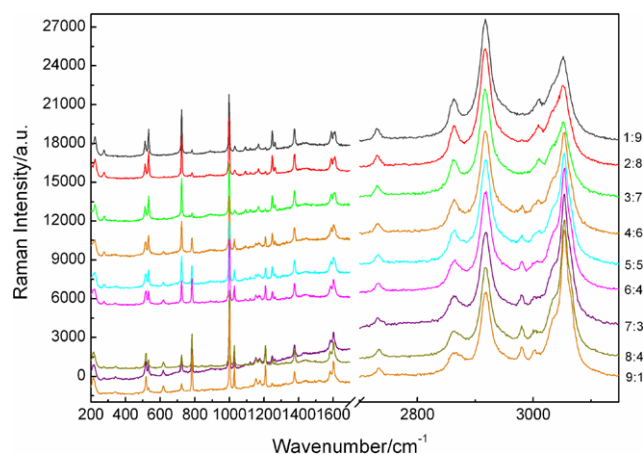


Fig. 3 Spontaneous Raman scattering spectra of a binary solution at different volume concentrations. $V_{\text{Tol}} : V_{\text{m-xyl}}$ is from 1 : 9 to 9 : 1

so the 1002 cm⁻¹ band is more easily stimulated than the 2920 cm⁻¹ and 3058 cm⁻¹ bands when the volume concentrations of toluene are 90%, 80%, 20% and 10%. The spontaneous Raman scattering intensities (peak areas in Fig. 3) of the 2920 cm⁻¹ and 3058 cm⁻¹ bands are similar when the volume concentration of toluene is 50%, which means that the spontaneous Raman intensities of the 2920 cm⁻¹ and 3058 cm⁻¹ bands of toluene are equal to the m-xylene, respectively. The RSCS values of both peaks will be dramatically changed depending upon the different volume concentrations, and so will be peak maxima. Because the intermolecular Fermi resonance exists on both the 2920 cm⁻¹ band and the 3058 cm⁻¹ band between toluene and m-xylene, it increases the RSCS values of both bands and simultaneously decreases the first-order Stokes thresholds of both bands in the binary solution. There is Raman mode competition between the 1002 cm⁻¹ and the 2920 cm⁻¹ and 3058 cm⁻¹ bands; the 2920 cm⁻¹ and 3058 cm⁻¹ bands are dominant in the competition, which results in the first- and second-order Stokes thresholds of the 1002 cm⁻¹ band to become higher, and suppresses the growth of the first- and second-order stimulated Raman peaks of the 1002 cm⁻¹ band from individual solvents. When the volume concentration of toluene is 50%, the RSCS values of the 2920 cm⁻¹ and 3058 cm⁻¹ bands are the largest, and the scattering power is the strongest, which leads to the second-order stimulated Raman peak of the 1002 cm⁻¹ band cannot be generated in the experimental laser energy range (0–5 mJ). According to Fig. 2 and Table 2, if the RSCS value of the 2920 cm⁻¹ band is larger than the 3058 cm⁻¹ band, the 2920 cm⁻¹ band is the main Stokes peak, or else the 3058 cm⁻¹ band is the main Stokes peak, since the different volume concentrations result in the different Fermi resonance intensities, which make the strong Fermi resonance peak become the main Stokes peak. There is a stimulated Raman peak at 1002 cm⁻¹ in Fig. 2 and its inten-

Table 2 The RSCS values of the 2920 cm⁻¹ and 3058 cm⁻¹ bands with different volume concentrations

$V_{\text{Tot}} : V_{\text{m-xy}}$	RSCS of 2920 cm ⁻¹ (10 ⁻²⁹ cm ² molecule ⁻¹ Sr ⁻¹)	RSCS of 3058 cm ⁻¹ (10 ⁻²⁹ cm ² molecule ⁻¹ Sr ⁻¹)
1 : 9	0.861	0.623
2 : 8	1.402	1.021
3 : 7	3.724	3.520
4 : 6	6.863	6.126
5 : 5	14.425	14.024
6 : 4	6.040	6.767
7 : 3	3.014	3.928
8 : 2	1.089	1.530
9 : 1	0.713	0.866

sity varies with the volume concentration as well. The anti-Stokes spontaneous Raman scattering is associated with the heat-populated high-energy levels of the solvents, but the SRS process is not limited by the heat-populated energy levels [26]. The stimulated Raman anti-Stokes scattering is a stimulated four-photon mixing process, $\omega_{\text{anti-Stokes}} = 2\omega_{\text{laser}} - \omega_{\text{Stokes}}$, so its intensity varies with the first-order Stokes intensity of the 1002 cm⁻¹ band, that is to say, the first-order anti-Stokes intensities of the 1002 cm⁻¹ band vary with the concentration ratio.

The multi-bands of stimulated Raman spectra can even be changed to another wavelength by using liquids with different typical vibrations, which should pave a new simple way for supercontinuum generation at selective wavelengths. And, the intermolecular Fermi resonance has potential application in intermolecular science.

4 Conclusion

SRS of the 1002 cm⁻¹, 2920 cm⁻¹ and 3058 cm⁻¹ bands were simultaneously generated in the binary solution of toluene and m-xylene, and the main peaks of the 2920 cm⁻¹ and 3058 cm⁻¹ bands are different with varying volume concentrations. The main mechanism of these phenomena is the intermolecular Fermi resonance, which is verified by the RSCS theory. Intermolecular Fermi resonance can stimulate Raman peaks while suppressing Raman peaks from individual solvents; it make RSCS values of Fermi peaks become larger and increases the SRS thresholds of individual solvents. The multi-bands of SRS can be used to generate supercontinuum radiation, and the intermolecular Fermi resonance has potential application in intermolecular science.

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