Research on Raman spectrum in liquid core optical fiber of CCl$_4$ solution

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The Raman spectrum intensity can be enhanced in liquid core optical fiber (LCOF) of CCl$_4$ solution. We dissolved liquid CCl$_4$ into CS$_2$ and got solutions of different concentrations. There is an optimum concentration at which the maximum Raman intensity can be obtained. There exists an optimum fiber length of 2 m. The experimental result is in good agreement with the theoretical calculation. The Raman intensity becomes powerful with the increase of the pump power and Raman linewidth becomes narrower with the decrease of the CCl$_4$ concentration.

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Raman spectrum technology is an important part of spectroscopy. Various technologies of enhancing Raman scattering signal are studied, such as fluorescence enhancement of stimulated Raman scattering (SRS)[1], liquid core optical fiber (LCOF) technologies, and so on. Since LCOF of benzene core was made in American Bell Laboratory in 1970s, LCOF was used widely in many science areas. The reason for using LCOF is that laser can transmit in LCOF, and contact with the sample sufficiently. Since the fiber may be many meters long, much more Raman scattering light can be produced and collected compared with the conventional systems. Raman intensity can be improved[2−4].

LCOFs are used in many areas due to Raman spectral effect, including 1) environment monitoring, which necessitates the ability to detect low-level analyte concentrations in aqueous solutions; 2) reducing the cost of device, where the intensity enhancement provided by LCOFs might enable the use of less expensive lasers and detectors; 3) high-performance liquid chromatogram, where convenient geometry, small volume, improved signal intensity, and signal-to-noise ratio (SNR) make Raman detection attractive; 4) biological applications, where low solubility and denaturing at high laser power often mandate the use of nonstandard sampling techniques[5].

During a pumping photon interacting with the fiber molecules, there is a frequency shift[6] between the pumping and scattering photons, as shown in Fig. 1. The scattering photons of molecules are separated into two types:
i) Stokes scattering photon

$$hv_{\mathrm{s}} = hv_{\mathrm{p}} - h\Delta v; \qquad (1)$$

ii) anti-Stokes scattering photon

$$hv_{\mathrm{a}} = hv_{\mathrm{p}} + h\Delta v, \qquad (2)$$

where h is Planck constant, v_{p}, v_{s} and v_{a} are pumping, Stokes scattering, and anti-Stokes scattering photon frequencies respectively, Δv is frequency shift.

Figure 2 is the experimental setup diagram of measuring Raman spectrum of LCOF. Backward pump is used

and Backward Raman scattering spectrum of LCOF is measured. There are higher SRS signal and lower pumping laser power for backward pumping compared with the forward pumping in our experiment. This is in according to the simulation results of Ref. [7]. But higher pumping power results in liquid gasification and signal instability. The setup includes several sections as follows: 1) LCOF. The internal diameter of hollow core silica optical fiber is 135 μm. It is filled with the solution of different concentrations which is composed of CS$_2$ and CCl$_4$, and ended with a container filled with the solution. 2) Single mode fiber (SMF). The core diameter of single mode fiber is 9 μm and the cladding diameter is 125 μm. Since the cladding diameter of SMF is smaller than the internal diameter of LCOF, SMF can be inserted into LCOF directly. 3) Coarse wavelength division multiplexer (CWDM). A CWDM of model 1427/1520 is adopted. 4) Pump source (a fiber Raman laser). Its
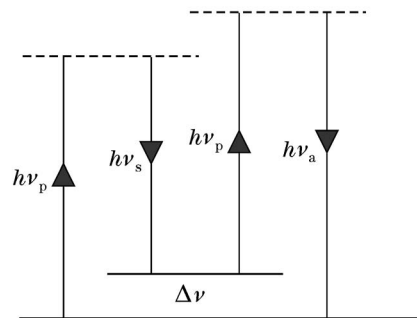

Fig. 1. Diagram of molecular vibration energy level and Raman scattering.
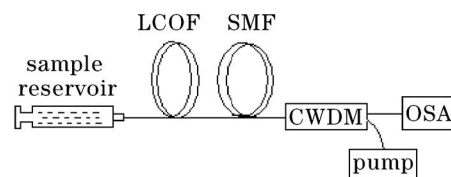

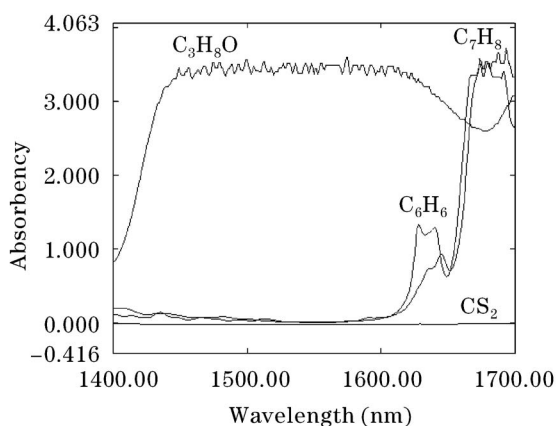Fig. 2. Experimental setup of measuring Raman spectrum of LCOF.

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Fig. 3. Absorption spectra of C_6H_6, C_7H_8, C_3H_8O, and CS_2.

wavelength is 1427.2 nm and bandwidth is 0.067 nm. Tunable range of output power is from 1 to 1200 mW. 5) Optical spectrum analyzer (OSA). Its spectrum range is 600—1700 nm, resolution is 10 pm and dynamic range is 60 dB. The result shows that the frequency shift of Raman peak for CCl_4 is 459 cm^{-1}.

The Raman spectrum intensity of CCl_4 ($n_{CCl_4} = 1.457$) is largest among the researched solutions. Unfortunately, the refractive index is smaller than that of quartz cladding ($n_{quartz} = 1.460$). Therefore, the enhanced optical fiber Raman spectrum can not be acquired directly. So we must choose a solvent whose refractive index is larger than quartz, such as C_6H_6, C_7H_8, C_3H_8O, and CS_2. Attenuation spectra of these liquids were measured as shown in Fig. 3. The attenuation of the light in CS_2 is small in the range from 1400 to 1700 nm. So, we dissolved liquid CCl_4 into CS_2 and got different concentration solution.

We measured the refractive index with a series of different CCl_4 concentrations from 0% to 100% (volume proportion). The relation between the refractive index n_{core} and CCl_4 concentration c is

$$n_{core} = -0.157c + 1.60936. \tag{3}$$

Raman scattering light occurs in all directions, only the portion light within the acceptance angle undergoes total internal reflection and transmits in the core. Numerical aperture (NA) represents the ability of receiving light in fiber. The relation between NA and n_{core} is

$$NA = \sqrt{(n_{core})^2 - (n_{clad})^2}, \tag{4}$$

where n_{core} and n_{clad} are the refraction indexes of the liquid core and quartz cladding, respectively. When NA is bigger, the ability of receiving light is more powerful and verse versa. The NA of LCOF will decrease with increasing solution (analyte) concentration, resulting in a decreased Raman signal. The light signal is proportion to the square of NA. Secondly, Raman scattering light is also influenced by the number of solute (analyte) molecules, it is proportion to the analyte concentration directly. Therefore, Raman scattering light intensity I can be known as[8]

$$I \propto NA^2 \cdot c. \tag{5}$$

From Eqs. (3),(4), and (5), we get the following formula

$$I \propto 0.025c^3 - 0.505c^2 + 0.458c. \tag{6}$$

The optimal concentration can be calculated by $\partial I/\partial c = 0$. It is 0.46.

The measurement of Raman intensity is made according to Fig. 2. Firstly, when pumping laser power is smaller (for example 1 mW), Raman scattering signal is thought as spontaneous Raman scattering signal $S_{small}(\lambda)$. $S_{small}(\lambda)$ for definite wavelength band (such as 1480—1680 nm) is displayed and memorized in OSA. Secondly, when pumping laser power is bigger (≥ 100 mW), Raman scattering signal is thought as stimulated Raman scattering signal $S_{big}(\lambda)$. $S_{big}(\lambda)$ is displayed in OSA. The relative Raman intensity $S_R(\lambda)$ is

$$S_R(\lambda) = S_{big}(\lambda)/S_{small}(\lambda). \tag{7}$$

The smaller and bigger pumping laser powers are the same for different concentration solutions. So, we can measure relative Raman intensity of LCOF in definite wavelength band. The maximum relative Raman intensity is in 1527 nm or the SRS frequency shift of 459 cm^{-1}. Figure 4 shows the comparison between the measurement and the calculation of normalized Raman intensity for 1527 nm. The calculated values are in excellent agreement with the experiment results.

In experiment, the stability is worse with the pump power increasing for the bigger analyte concentration. As long as the pump power is more than 0.5 W, the detected noise is larger and SNR decreases. However, when the concentration is smaller, higher pump power can be put into the fiber and stronger Raman peak can be obtained. It is because that 1) when high pump power is coupled into the fiber, the solution tends to be gasified due to higher concentration of CCl_4; 2) when the analyte concentration is higher, the NA is lower, then the ability of receiving light in fiber is lower, and it is difficult to detect Raman scattering light.

The intensification of Raman scattering light dI_R in the fiber length dx is given by

$$dI_R(x) = G_R I(x)dx - \alpha I_R(x)dx, \tag{8}$$

where G_R is Raman gain coefficient which is related to Raman scattering cross section, I_R and I are the Raman and pumping intensities respectively, and α is the loss coefficient for light travelling in the fiber. If it is assumed that the loss coefficient in the fiber is the same at the wavelength of Raman or pumping radiations, and
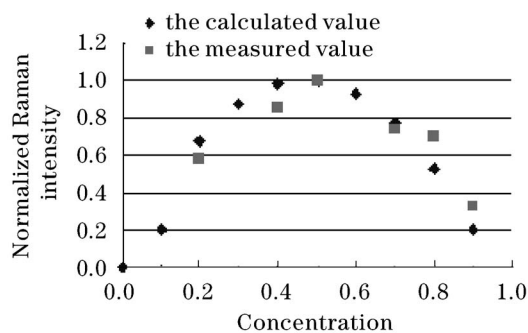

Fig. 4. Comparison between the measurement and the calculation of Raman intensity.

that the amount of light converted to Raman radiation is smaller, then

$$I(x) = I_0 e^{-\alpha x}, \qquad (9)$$

where I_0 is the intensity of the pumping light at $x = 0$. Substituting Eq. (9) into Eq. (8), we can obtain

$$I_R = \int_0^x dI_R(x) = G_R I_0 x e^{-\alpha x}. \qquad (10)$$

From it, we can conclude that Raman intensity increases to a maximum with increasing fiber length firstly, then decreases because the fiber attenuation becomes dominant. Therefore, there is the optimum fiber length by $dI_R/dx = 0$ and the optimum length L is $1/\alpha$.

We measured Raman intensity of 459 cm^{-1} Raman shift along with the change of fiber length. The results are listed in Table 1. When the fiber length is 2 m, Raman intensity is the largest. Meanwhile, we can know that Raman intensity increases with the increase of the pump power.

Raman linewidth (full width at half-maximum) of solution CCl$_4$ is narrower compared with silica (several hundred wave numbers). The linewidth of CCl$_4$ is influenced by concentration. So, the linewidth relates to the number of molecules. The movement between different kinds of molecules make rotating in molecules disappear, and perhaps the two rotating states exit many transitions, which determines the width of vibration linewidth. Fujiyama et al. showed that Raman linewidth becomes narrower when the concentration decreases[9]. This result is approved by our experiment. For different CCl$_4$ concentrations, Raman intensity and linewidth are measured according to Fig. 2 and Eq. (7). When the concentrations are 20%, 50%, and 90%, Raman linewidths are 1.38, 1.73, and 1.89 nm, as shown in Figs. 5(a), (b), and (c), respectively. From it, we can see that Raman intensity of 50% CCl$_4$ concentration is better than that of 20% and 90% CCl$_4$ concentrations, simultaneously.

Table 1. Raman Intensity Relation with the Fiber Length (L) and Pump Power (P) (Arbitrary Unit)

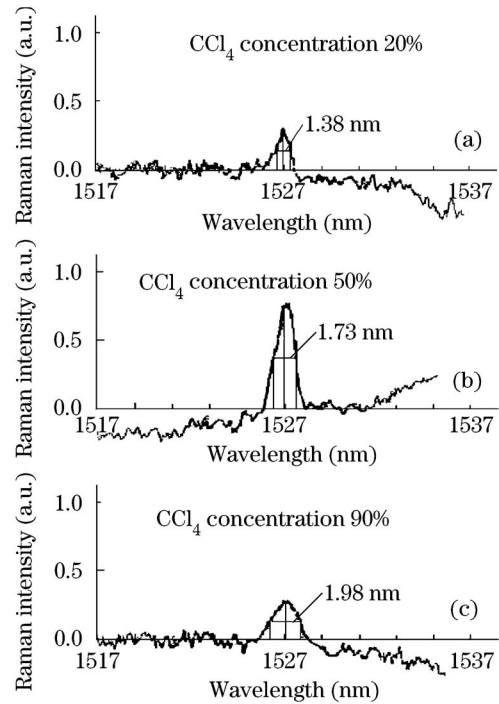| P (W)	L (m)				
	1	2	3	4	5
0.5	0.42	0.44	0.45	0.42	0.45
0.6	0.50	0.52	0.49	0.48	0.46
0.7	0.57	0.59	0.57	0.56	0.54
0.8	0.61	0.64	0.62	0.58	0.56
0.9	0.64	0.69	0.65	0.62	0.65
1.0	0.72	0.74	0.72	0.71	0.71

Fig. 5. Raman linewidth changed with different concentrations.

SRS in LCOF makes the efficiency of Raman increase. It is used to enhance the sensitivity of concentration analysis, it is also possible to study and design LCOF Raman amplifier.

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