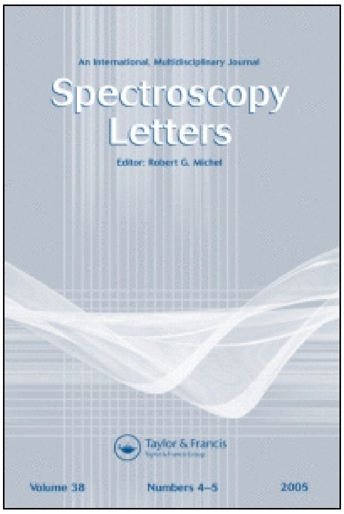

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EFFECT OF OPTICAL FIBER LOSS ON RESONANCE RAMAN SPECTRA OF SAMPLES WITH LOW CONCENTRATION

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ABSTRACT

The resonance Raman effect which is produced in a liquid-core optical fiber can enhance the Raman spectral intensity 10^9 times. The optimum length of the optical fiber depends on the sample concentration, modal absorption coefficient, scattering coefficient, coupling coefficient, and molar absorptivity. A sample with a lower concentration is preferred. We obtained the Raman spectra of samples with low concentrations 1×10^{-15} mol/L (I_2 in CS_2) and 0.8×10^{-16} mol/L (β-carotene in CS_2).

Key Words: Liquid-core optical fiber; Resonance Raman spectrum; Waveguide

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INTRODUCTION

The resonance Raman scattering effect has been applied to various areas involving the study of molecular structure and the analysis of component and concentration[1–4]. Nevertheless, to observe the resonance Raman effect, a high power laser is needed, which tends to destroy the molecular structure of samples. Liquid-core optical fiber is made of a capillary full of high refractivity transparent liquid. Since its beginning, significant accomplishments have been obtained in nonlinear optics[5] and molecular structure study[6]. It is reported that the Raman spectrum intensity can be enhanced 10^3 times by means of a liquid-core optical fiber[7–8]. Moreover, the Raman spectrum intensity can be enhanced 10^6 times using a resonance Raman technique. Hence, if the resonance Raman effect is produced in a liquid-core optical fiber, the Raman spectrum intensity can be enhanced 10^9 times ($10^3 \times 10^6 = 10^9$). The conventional resonance Raman spectrum technique has been researched widely, while the resonance Raman spectra obtained by using optical fiber has not been studied as thoroughly. In our experiments, we investigated the resonance Raman spectra in optical fiber and observed the resonance Raman spectra of I_2 in CS_2 and β-carotene in CS_2, whose intensity has been enhanced by 10^2 to 10^3 times. The study shows that the intensity of the Raman spectra depends on the wavelength (frequency) of the excitation laser and the optical fiber length. This optimized fiber length correlates with sample concentration, molar absorptivity, modal absorption coefficient, scattering coefficient, and coupling coefficient. We also obtained the Raman spectra of samples with low concentrations 1×10^{-15} mol/L (for I_2 in CS_2) and 0.8×10^{-16} mol/L (for β-carotene in CS_2), 6–8 orders of magnitude lower than were detected with a conventional capillary. In this paper, the experimental method of obtaining resonance Raman spectra in a liquid-core fiber waveguide is given and the experimental results are discussed.

EXPERIMENTAL

β-carotene and I_2 were dissolved in CS_2 respectively and were diluted to various concentrations. In order to understand the sample absorption, we detected the ultraviolet-visible absorption spectra of β-carotene in CS_2 and I_2 in CS_2 using a Shimadzu UV-240 spectrometer. The solutions of various concentrations of β-carotene in CS_2 and I_2 in CS_2 were filled into hollow-core optical fibers with an inner diameter of 200 μm. To prevent the liquid from flowing and to keep the liquid stable, both ends of the optical fiber were sealed with a special "seal cell" consisting of windows and a low pressure gas which can prevent the swelling and breakage of the liquid-core optical fiber when the temperature changes. In the experiment, we used a typical spectroscopic apparatus consisting of an Ar^+ laser and a spectrometer, Spex 1403, equipped with a cooled photon multiplier and photon counting electronics for the signal processing. The wavelengths of exciting light were 514.5 and 488.0 nm. The laser enters into one end of the liquid-core optical fiber, and the Raman signal was measured on the other end. We have performed experiments on various optical fiber lengths with various concentrations (for I_2 in CS_2 and β-carotene in CS_2). For comparison, we have also measured the resonance Raman spectra of β-carotene in CS_2 with the conventional capillary method.

RESULTS AND DISCUSSION

The Dependence of the Optimal Optical Fiber Length on the Sample Concentration, Molar Absorptivity, Modal Absorption Coefficient, Scattering Coefficient, and Coupling Coefficient

The incident laser propagates along the liquid-core optical fiber. When the stimulated effects are neglected, the intensity of resonance Raman scattering signal $I_{RR}(x)$ in the optical fiber is given in the differential form as

$$dI_{RR}(x) = G_{RR}(v_o, v_i)I(x)dx - a_i I_{RR}(x)dx \qquad (1)$$

where $G_{RR}(v_o, v_i)$ is the resonance Raman gain coefficient related to the exciting frequency v_o and scattering frequency v_i; $I(x)$ is the intensity of the exciting laser which decays with the optical fiber length x in the form of $I_o \exp(-a_o x)$ (and where a_o is the loss coefficient for exciting light); a_i is the loss coefficient for the Raman light; a_o, a_i correlate with the concentration of sample, the molar absorptivity (for the specific spectral band of interest), and the structure of the hollow-core optical fiber. Substituting $I(x) = I_o \exp(-a_o x)$ into Eq. (1), we can obtain

$$dI_{RR}(x) = G_{RR}(v_o, v_i)I_o \exp(-a_o x)dx - a_i I_{RR}(x)dx \qquad (2)$$

The solution for Eq. (2) is

$$I_{RR}(x) = G_{RR}(v_o, v_i)I_o[\exp(-a_o x) - \exp(-a_I x)]/(a_i - a_o) \qquad (3)$$

Using Eq. (3), we can obtain the optical length which yields the optimum Raman intensity. When $dI_{RR}/dx = 0$, $I_{RR}(x)$ realizes its maximum value. Thus the optimum length of the optical fiber is

$$\mathrm{L} = \ln(\mathsf{a}_o/\mathsf{a}_i)/(\mathsf{a}_o - \mathsf{a}_i) \tag{4}$$

According to optical fiber theory, the light loss of a liquid-core optical fiber results from the absorption, scattering, the modal coupling, and so on. Wei Lei and Wang Wei et al.[6,9,10] studied the relationship of the absorbance (the tall loss of an optical fiber) A and the optical fiber length Z, sample concentration C, modal absorption coefficient a_1, scattering coefficient β_1, and coupling coefficient d_o. The absorbance A of the optical fiber is

$$\mathrm{A} = \varepsilon cz + \log\left[\frac{Ch[2z\sqrt{D(\alpha_1\varepsilon c + \beta_1)}] + \frac{\omega^2}{2}\sqrt{(\alpha_1\varepsilon c + \beta_1)/D}Sh[2z\sqrt{D(\alpha_1\varepsilon c + \beta_1)}]}{Ch(2z\sqrt{\beta_1 D}) + \frac{\omega^2}{2}\sqrt{\beta_1/D}Sh(2z\sqrt{\beta_1 D})}\right] \tag{5}$$

where

$$D = \left(\frac{\lambda}{4na}\right)^2 d_o$$

and where ε is the molar absorptivity of the sample for the light, α is the radius of the optical fiber core, n is the refractive index of the core liquid, λ is the exciting laser wavelength, ω is the area of the Gauss beam. From Eq. (4) and Eq. (5), we can conclude that the optimal length of optical fiber depends on the sample concentration c, modal absorption coefficient a_1, scattering coefficient (β_1), coupling coefficient (d_o), and the molar absorptivity (ε).

Considering that the coupling coefficient of the liquid-core optical fiber is 2 orders of magnitude smaller than that of a quartz optical fiber[11], and the sample concentration studied by here is rather low, the modal coupling coefficient and the scattering coefficeint can be neglected. Thus when $\beta_1 = 0$, and $d_o = 0$, then Eq. (5) becomes

$$\mathrm{A} = \mathrm{c}\varepsilon\mathrm{z} = \mathsf{a}z \tag{6}$$

In Eq. (6), a is the loss coefficient of an optical fiber for light propagating into it; $\mathsf{a}_o(\mathsf{a}_o = \varepsilon_0 c)$ and $\mathsf{a}_i(\mathsf{a}_i = \varepsilon_i c)$ are the loss coefficients of an optical fiber for the exciting light and for the Raman light. Eq. (4) can be expressed as

$$\mathbf{L} = \frac{\mathbf{1}}{\mathbf{c}(\varepsilon_0 - \varepsilon_1)}\mathbf{ln}\frac{\varepsilon_0}{\varepsilon_1} \tag{7}$$

From Eq. (7), it is evident that the optimum length of the liquid-core optical fiber depends on the concentration and the molar absorptivity of the sample. The relationship between the concentration and the optimal length for the 1520 cm^{-1} Raman band of β-carotene in CS_2 is shown in Fig. 1. In Fig. 1, the curve (a) is described by Eq. (7), and (b) is the experimental curve. The discrepancy between curve (a) and curve (b) is due to the structural defect of

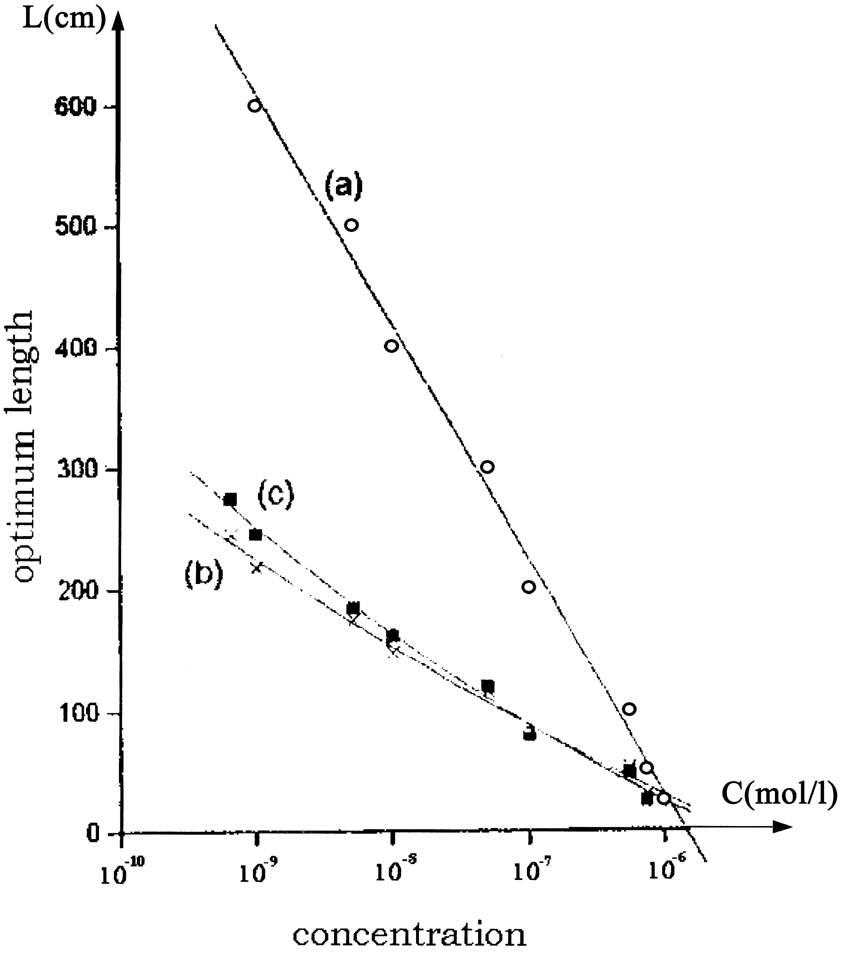

Figure 1. The relation of the optimum length and the sample concentration of 1520 cm^{-1} Raman line of β-carotene in CS_2. (a), ○ is the calculated curve [using the Eq. (7)], (b) × is the experimental curve. (c), ■ is the calculated curve using Eq. (7) and taking into account the structure loss of the optical fiber used in the experiment.

the hollow-core optical fiber used in this experiment. The loss coefficient of the optical fiber used in the experiment is about $5\times10^{-3}\,\mathrm{cm}^{-1}$ larger than the theoretical value ($10^{-4}\,\mathrm{cm}^{-1}$). Taking the structural loss into account, we obtained curve (c) using Eq. (7). Curve (c) is in good agreement with the experimental curve (b). On the basis of Eq. (7), we obtained good quality resonance Raman spectra of I_2 in CS_2 and β-carotene in CS_2, where the intensity of the resonance Raman spectra has been enhanced 10^2–10^3 times higher than that obtained using a conventional capillary with the same experimental conditions (Fig. 2).

An Efficient Method of Trace Analysis and Structure Study of Molecular with Low Concentration

The resonance Raman spectrum intensity can be enhanced 10^2 to 10^3 times using a liquid-core optical fiber. This technique has extensive applications, including the study of molecular structure (for example, the research of biomolecules under liquid conditions), trace analysis, and so on. It is preferred that a sample in low or very low concentration is prepared. From Eq. (7), the optimum length of the liquid-core optical fiber depends on the concentration of sample and the molar absorptivity for the exciting light and for the Raman band. It is noted that when the sample concentration is low enough the absorption loss due to sample is very small. Furthermore, the absorption loss of sample for the exciting light is equal to that of sample for a Raman light. Thus, the total loss coefficient of the optical fiber for exciting light is equal to that for Raman light. That means, $\alpha_o = \alpha_I = \alpha$. Substituting $\alpha_o = \alpha_I = \alpha$ into Eq. (2), we obtain the solution:

$$\mathbf{L} = \frac{\mathbf{1}}{\boldsymbol{\alpha}} \tag{8}$$

From Eq. (8), it is evident that the optimum length of a liquid-core optical fiber is the reciprocal of the total loss coefficient. When the concentration of sample is very low, the total loss coefficient of the optical fiber is mainly due to the structural defects of the optical fiber (for example, the inside diameter is nonuniform, the inside face is rough and so on).

By developing a low loss optical fiber, we can increase the optimum length of optical fiber. In the meantime, if multi-time averaged values of measurements are obtained by the computer, we believe the intensity of resonance Raman spectra can be enhanced to an even greater extent. This technique of resonance Raman spectra in optical fiber has potential applications in the study of molecular structure and trace analysis. We have

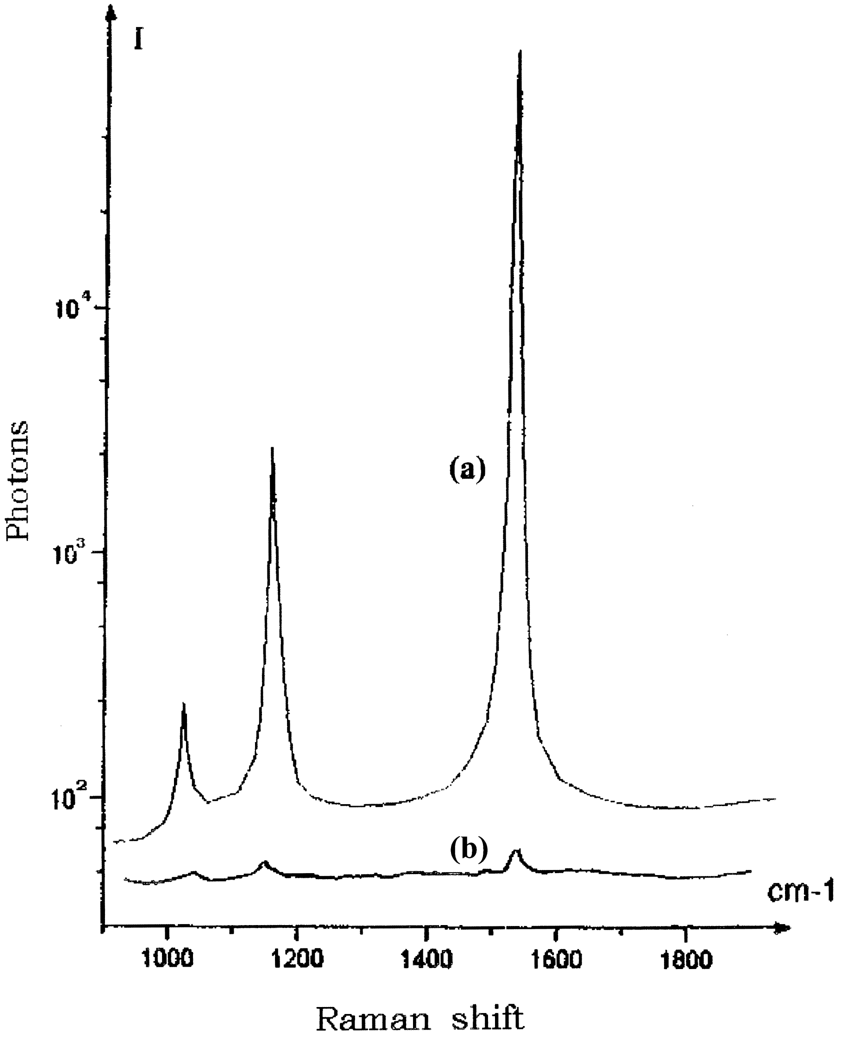

Figure 2. The resonance Raman spectra of β-carotene in CS_2 taken with (a) the 1.40 m liquid-core optical fiber; (b) the capillary. The concentration: 1×10^{-8} mol/L, the exciting wavelength: 514.5 nm, the exciting power: 30 mw.

studied trace analysis by means of this technique, obtained satisfactory Raman spectra of I_2 in CS_2 and β-carotene in CS_2 at the room temperature, with concentrations of 1×10^{-15} mol/L and 0.8×10^{-16} mol/L respectively (Fig. 3, Fig. 4).

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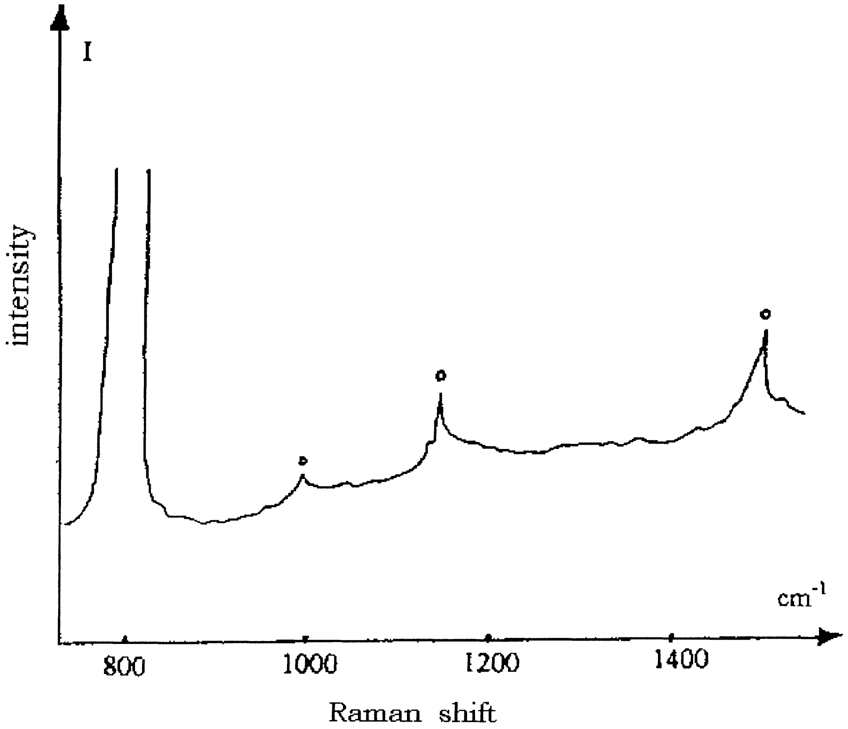

Figure 3. The optical fiber Raman spectra of I_2 in CS_2. The length of liquid-core optical fiber is 3.25 m, the exciting laser power is 30 mw, the exciting wavelength is 488.0 nm, the concentration is 1×10^{-15} mol/L.

CONCLUSION

When the resonance Raman effect is produced in the liquid-core optical fiber, the Raman spectra intensity can be enhanced 10^9 times. The method of obtaining resonance Raman spectra in optical fiber expands the range of applications for liquid-core optical fiber. It is possible to measure opaque (absorbent) samples easily by using this optical fiber technique. By providing a new experimental method, this technique has the potential for investigations pertaining to the state-change of micromolecules; the study of molecules interacting under liquid conditions; research relating to the structure of biomolecules (enzymes) in water, and other experiments not previously possible. We expect optimistically that this technique of

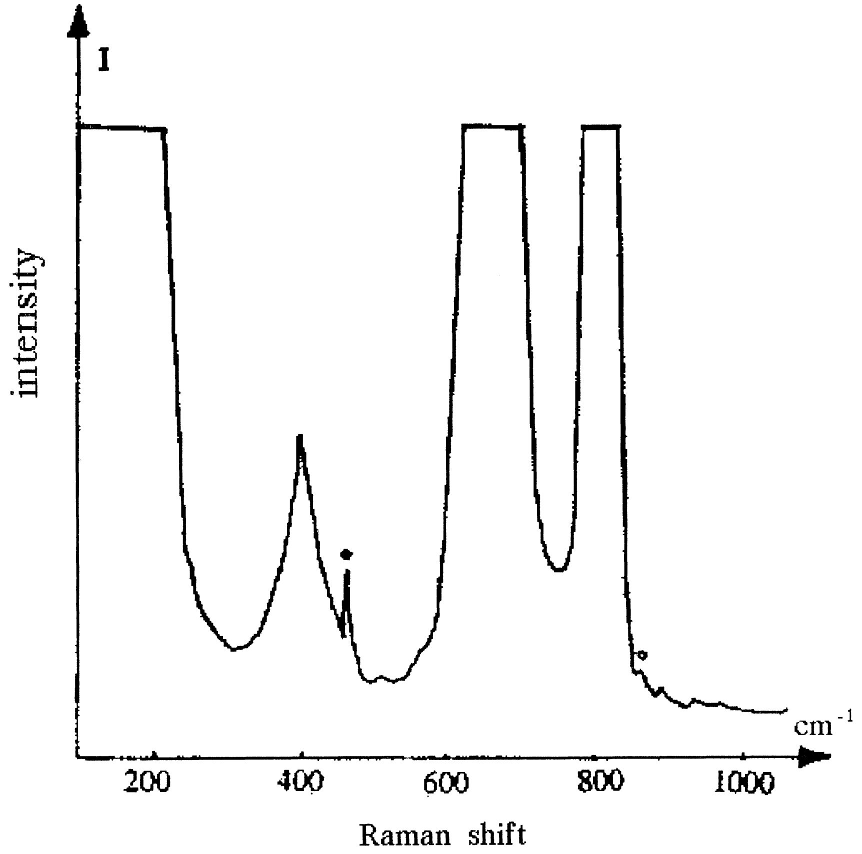

Figure 4. The optical fiber Raman spectra of β-carotene in CS_2. The length of liquid-core optical fiber is 2.72 m, the exciting laser power is 30 mw, the exciting wavelength is 514.5 nm, the concentration is 0.8×10^{-16} mol/L.

resonance Raman spectra in optical fiber can play an important role in the study of molecular structure and in trace analysis.

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