Low-loss liquid-core optical fiber for low-refractive-index liquids: fabrication, characterization, and application in Raman spectroscopy

R. Altkorn, I. Koev, R. P. Van Duyne, and M. Litorja

We describe a liquid-core optical fiber based on capillary tubing of Teflon AF 2400, which is a clear, amorphous fluoropolymer having a refractive index of 1.29. When filled with virtually any transparent liquid, the fiber is capable of transmitting light by total internal reflection. Loss below 3 dB/m is demonstrated throughout much of the visible region for a 250-μm-i.d. fiber filled with water. The utility of this device in enhancing the intensity of Raman spectra of core liquids is demonstrated. © 1997 Optical Society of America

Key words: Liquid-core optical fiber, Raman spectroscopy, Teflon AF.

1. Introduction

Light guiding in liquids was first studied scientifically in the mid 19th century, when Colladon,[1,2] Babinet,[1] Tyndall,[1,3] and others[1] investigated light propagation by total internal reflection in streams of water. By the end of the century, the effect had become quite widely known, largely because of its use in illuminated fountains.[1,4] However, interest in liquid light guides dwindled in the 20th century until approximately 1970, when workers in the US,[5] the UK,[6] and in Australia[7] began considering liquid-core optical fibers as potential communications media. A number of liquid-core fibers, consisting of small-diameter glass tubes filled with high-refractive-index liquids, were developed. They performed well, exhibiting losses below 8 dB/km in the near infrared[6,7] but were superseded by solid optical fibers that offered not only clear practical advantages but ultimately much lower loss.[8]

Although liquid-core fibers were never utilized in communications, it was demonstrated during the course of their development that they offer great advantages over conventional experimental apparatus in stimulated[9] and in spontaneous[10] Raman spectroscopy. For example, it was shown that confining the excitation radiation and efficiently collecting Raman-scattered light over long interaction lengths make it possible for liquid-core fibers to produce intensification factors of as much as 1000–3000 over conventional sampling arrangements in spontaneous Raman spectroscopy.[10] Significant advantages were later demonstrated in absorption[11] and in fluorescence[12] applications. Fibers consisting of glass capillaries filled with high-refractive-index liquids continue to be used in nonlinear optics.[13] However, in spite of their demonstrated advantages, they currently receive relatively little attention in linear spectroscopic applications. This is because the high refractive indices of silica-based glasses ($n \geq 1.46$), coupled with the requirement for total internal reflection that the refractive index of the core liquid exceed that of the capillary wall, severely limit their utility. The majority of liquids, including important solvents such as water, methanol, and acetonitrile, have refractive indices well below those of silica-based glasses. Nevertheless, the potential of waveguide sampling in spectroscopy has been widely recognized, and a number of devices capable of guiding light through liquids of lower refractive index have been developed. Most of these fall into one of

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the following categories: (i) glass or fused-silica tubes coated with reflective metals, (ii) bare glass or fused-silica tubes that have been cleaned to permit light transmission by means of total internal reflection at the outer (glass–air) interface, (iii) tubes coated internally or externally with low-refractive-index polymers, and (iv) plastic tubes. We briefly discuss each class of device below.

Waveguides based on highly reflective metals are routinely used in the microwave and infrared regions and have been successfully applied in visible absorption spectroscopy.[14–18] They have the advantages of guiding light through any transparent core liquid (or gas) regardless of refractive index and, in principal, collecting light over a very large solid angle. However, most devices reported to date have been characterized by a high loss that makes them ill-suited to fluorescence or Raman applications. For example, Tsunoda *et al.*[16,17] measured a loss of approximately 250 dB/m at 632.8 nm for 340-μm-i.d., 520-μm-o.d. externally silvered glass tubes filled with water. Recent research indicates that loss can be significantly reduced,[19] although not to levels demonstrated in waveguides based on total internal reflection.

Liquid-core waveguides made of uncoated glass capillaries were first used in Raman spectroscopy by Schwab and McCreery[20,21] and in absorption applications by Tsunoda *et al.*[16,17] These devices, which guide light by means of total internal reflection at the glass–air interface, represented perhaps the most significant development in water-based light guides since the original work of Colladon[2] in 1842. They were the first water-filled waveguides to offer low loss (values of 18 and 8 dB/m at 632.8 nm were demonstrated by Tsunoda *et al.*[17] for 340 μm-i.d., 520 μm-o.d. and 215 μm-i.d., 360 μm-o.d. borosilicate-glass tubes filled with water), and, for this reason, they have achieved relatively widespread use in diverse spectroscopic applications. They have been used successfully not only in Raman spectroscopy,[20–22] but in fluorescence[23–25] and in absorption[16,24,25] applications as well, and are used to enhance other analytical techniques, including high-performance liquid chromatography[24] (HPLC) and capillary electrophoresis.[25]

In spite of their excellent performance, uncoated glass waveguides have several important disadvantages. As Tsunoda *et al.*[17] have discussed, their loss characteristics are largely determined by the condition of their outer surfaces. They must therefore be cleaned before use, be kept clean during use, be handled carefully to avoid scratching, and be used with end cells that do not compromise the optical quality of the glass–air interface in the sampling region by means of physical contact or leakage. Uncoated glass tubes are also quite fragile, particularly those having small diameters or thin walls.

In addition to these practical difficulties, uncoated glass waveguides have drawbacks from an optical point of view. Since they function through internal reflection at the external surface of the glass tube, they allow light to propagate through the tubing wall as well as the liquid core. In fact, much of the commercially available capillary tubing has a sufficiently high ratio of outside-to-inside diameter that this can be the dominant mode of propagation. For example, Tsunoda *et al.*[17] observed effective path lengths that were less than half the physical cell length in their work with 215-μm-i.d., 360-μm-o.d. tubing filled with water. From a spectroscopic point of view, propagation in the glass wall has several adverse consequences. In Raman studies, it results in the generation of silica bands, and although glass is a weak Raman scatterer and silica bands have not been problematic in studies to date, they are nevertheless present and will ultimately become the source of unwanted background. Propagation through the glass also increases the étendue of the waveguide without increasing the path length of light in the liquid.

Liquid-core fibers consisting of glass capillaries coated internally and/or externally with polymers offer several practical advantages over bare glass devices, including immunity to exterior surface contamination and, in the case of externally coated devices, improved flexibility and breakage resistance. Liquid-core fibers based on tubing lined with polymers have been reported by Gilby and Carson[26] and Dress and Franke,[27–29] who investigated glass tubes coated internally with Teflon AF 2400; and Hong and Burgess,[30] who used porous polypropylene tubes coated internally with Teflon AF 2400. Neither Gilby and Carson[26] nor Hong and Burgess[30] included measurements of the optical properties of their liquid-core fibers. Dress and Franke[29] reported loss as low as 1.6 dB/m at 632.8 nm for 3-mm-i.d. tubes filled with water, and they also provided a detailed mathematical model of light propagation in their waveguide.[28,29] A liquid-core waveguide based on externally coated silica tubing was recently reported by Altkorn *et al.*,[31] who obtained loss of approximately 1 dB/m over much of the visible region by using water-filled 530-μm-i.d., 630-μm-o.d. silica tubing coated with a thin layer of Teflon AF having a refractive index of 1.31. Although this device offers excellent transmission properties, it is quite fragile and retains the disadvantages associated with light propagation in the silica wall.

Liquid-core fibers based on plastic capillaries are in many respects the ideal choice for spectroscopic applications. They are extremely flexible and breakage resistant and contain light entirely within the core liquid. Most research to date on plastic waveguides has involved the perfluorinated polymers poly(tetrafluoroethylene) (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and poly(tetrafluoroethylene-co-perfluoropropylvinyl ether) (PFA), which have refractive indices of 1.35,[32] 1.34,[33] and 1.35,[32] respectively. In some cases excellent results have been obtained. For example, Tsunoda *et al.*[34] achieved losses as low as 0.57 dB/m at 632.8 nm, using 900-μm-i.d. FEP tubes filled with 99.5% ethanol ($n_D = 1.36$). Unfortunately, FEP as well as the other common fluoropolymers have refractive indices too high to permit light guiding through water ($n =$

1.33). The only commercially available plastics (and the only commercially available room-temperature solids from which liquid-core waveguides can reasonably be fabricated) capable of guiding light through water are the amorphous copolymers of tetrafluoroethylene and 2,2-bistrifluoromethyl-4,5-difluoro-1,3-dioxole,[35] sold by DuPont as Teflon AF. These materials have excellent optical clarity and very low refractive indices ($n = 1.31$ for Teflon AF 1600 and 1.29 for Teflon AF 2400). The refractive index of Teflon AF 2400 is lower than that of virtually all standard temperature and pressure liquids, and it is near the theoretical minimum for an organic polymer predicted by Groh and Zimmerman.[36]

In the present paper we describe a liquid-core optical fiber based on tubing made entirely of Teflon AF 2400. We show that this device can transmit visible light with low loss when filled with low-refractive-index liquids such as water, methanol, and ethanol. We believe that the loss characteristics, the water compatibility, and the robust nature of this device will make it of considerable value in diverse spectroscopic applications and will demonstrate its utility in enhancing the intensity of the Raman spectra of core liquids.

2. Experimental

The Teflon-AF 2400 capillary tubing used in this study was drawn from preforms in an optical-fiber draw tower. The size of the preforms (100 mm long × 25-mm o.d.) was restricted by the extremely high cost of the polymer ($10,000/kg). The preforms were produced by consolidation of Teflon-AF 2400 pellets. When a set of precisely controlled process parameters (time, temperature, vacuum, N_2 pressure) was used, it was possible to produce preforms free of voids and bubbles. Capillary tubing was drawn in a diminishing cone from the tip of a molten preform. The manufactured, water-clear, and highly flexible tubing had an o.d. of 525 μm and an i.d. of 250 μm with a variation of ±8% over the course of a run.

The liquid-core optical fiber was formed by the mounting of the Teflon-AF 2400 tubing onto previously described[31] end cells based on standard 1.59-mm (1⁄16-in.) HPLC tees, which allow both optical access and fluid transfer to the capillary. Light was coupled into the liquid-core fiber through a section of Polymicro Technologies FVP100110125 100-μm-core, 125-μm-o.d., 0.22 numerical aperture (NA), polyimide-coated silica optical fiber that was inserted into the tubing. The silica fiber was held in the tee with a 150-μm-i.d. PTFE tubing. Properly compressing the PTFE caused a liquid-tight sliding seal to be maintained. Light was coupled out of the liquid-core fiber with a 3M FT-400-UMT optical fiber, which has both a larger core diameter (400 μm) and NA (0.39) than a water-filled Teflon-AF capillary. The distance between the movable input fiber and the fixed output fiber set the effective length of the liquid-core fiber. We used a peristaltic pump fitted with silicone tubing to fill the liquid-core fiber, and we maintained flow throughout all experiments.

Three types of measurement were used for optical characterization of the liquid-core fibers: broadband (400–800-nm) loss spectra, attenuation at 632.8 nm versus effective liquid-core fiber length, and Raman spectroscopy of core liquids. This set of measurements was chosen to gauge the general utility of these fibers in spectroscopic applications. Loss along with étendue[37] (the product of the fiber area and the solid angle of emitted light) are the two most important optical quantities in most spectroscopic applications. In absorption spectroscopy, loss is equivalent to baseline attenuation and therefore governs the maximum length of fiber that can be used. In Raman (and fluorescence) research, intensity enhancement has been predicted to be inversely proportional to loss.[10]

Broadband loss measurements were performed with a Xe arc lamp (ACMI Model FCB-1002) and an optical spectrum analyzer (Instrument Systems Spectro 320) at a nominal 5-nm resolution. Spectra were recorded at two positions of the input optical fiber and loss was calculated as

$$\text{loss(dB/m)} = \frac{10}{L}\log_{10}\left(\frac{I_1}{I_2}\right),$$

where L is the effective cell length (which is equal to the distance between the two positions of the input fiber), I_1 is the intensity recorded when the input fiber is close to the output fiber, and I_2 is the intensity recorded when the input and the output fibers are further apart. Although this loss measurement technique is perhaps less common than conventional cutback methods, it was used because it is nondestructive and requires no manipulation of the end cells.

Attenuation at 632.8 nm was measured with a He–Ne laser (Uniphase Model 1125) and a powermeter (Newport Model 815 with 818-FA fiber adapter mount and FP3-CA3 SMA adapter). In these experiments, loss was determined when the position of the input fiber within the Teflon-AF tubing was adjusted in 0.05-m increments and the output power at each position was measured. Attenuation was calculated at each position as

$$\text{attenuation(dB)} = 10\log_{10}\left(\frac{I_0}{I}\right),$$

where I_0 is the light intensity measured when the input fiber is in physical contact with the output fiber and I is the output intensity at the given position of the input fiber. Loss in decibels per meter is given by the slope of attenuation versus the length. As discussed by Dahan *et al.*,[38] this technique has the advantage of identifying imperfections in the waveguide.

Raman measurements were performed in forward-scattering geometry by use of the 514.5-nm line of an argon-ion laser (Spectra Physics 2060), a 0.75-m

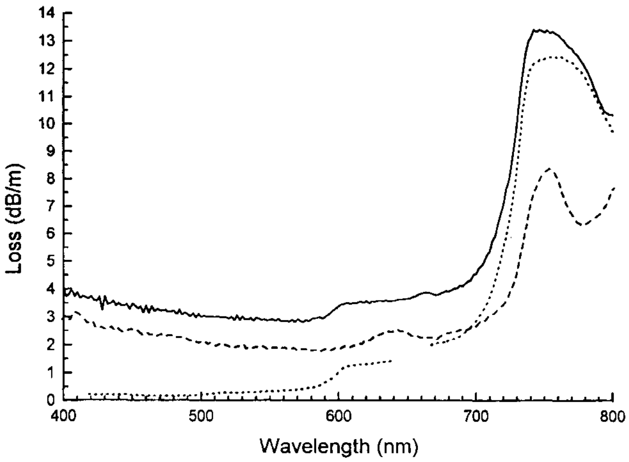

Fig. 1. Loss spectra of water (solid curve) and methanol (dashed curve) in a Teflon-AF 2400 capillary and in bulk water (dotted curve) from the data of Querry *et al.*[39] (between 418 and 640 nm) and Kou *et al.*[40] (between 667 and 800 nm).

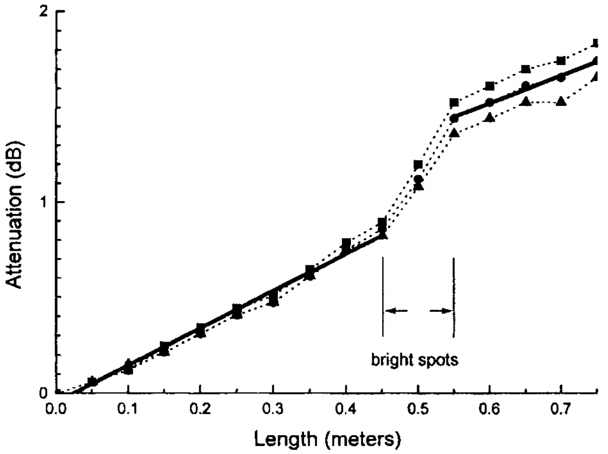

Fig. 2. Attenuation versus length in a Teflon-AF 2400 capillary filled with methanol (three sets of measurements). Solid lines show the least-squares fit to data between 0–0.45 and 0.55–0.75 m and indicate losses of 1.9 and 1.4 dB/m, respectively, in these regions.

scanning double monochromator (Spex 1400-II) set to 1 wave-number resolution (48-μm slits) and $F/1$ input optics. The liquid-core fiber assembly was the same as that used in the broadband loss and the He–Ne laser measurements. Light from the laser was focused into the input fiber, and all light exiting the output fiber was focused onto the entrance slit of the monochromator. No attempt was made to eliminate either laser radiation or silica bands generated in the input and the output fibers.

3. Results and Discussion

Broadband loss spectra of liquid-core fibers filled with water (Aldrich HPLC grade, $n_D^{20} = 1.3330$) and methanol (Fisher Optima grade, $n_D^{20} = 1.3288$) are shown in Fig. 1 along with spectra of bulk water taken from the data of Querry *et al.*[39] (between 418 and 640 nm) and Kou *et al.*[40] (between 667 and 800 nm). The spectra of water and methanol were acquired with different sections of Teflon-AF tubing. The effective length of the water–core fiber was 0.68 m and that of the methanol-filled fiber was 0.73 m. The data in Fig. 1 illustrate several characteristics of the liquid-core Teflon-AF fibers. It is seen that the water–core fiber exhibits loss below 3 dB/m throughout much of the visible region. To our knowledge, this is lower than that of any previously reported water-core fiber other than the much larger devices of Altkorn *et al.*[31] and Dress and Franke.[29] Nevertheless, it is still higher than would be expected for a perfect fiber in which loss was dominated by both absorption and scattering in the core. It is also seen that the methanol-filled fiber exhibits somewhat lower loss than does the water-filled fiber even though the refractive index of water is slightly higher than that of methanol. This is indicative of a trend observed during the course of this study: Teflon-AF fibers filled with organic solvents seem to perform somewhat better than those filled with water. It was also noted that the loss characteristics of liquid-filled Teflon-AF fibers vary somewhat between different sections of tubing. This is explained in part by the results of the measurements of attenuation versus length discussed below.

Attenuation at 632.8 nm as a function of position of the input optical fiber is shown in Figs. 2, 3, and 4 for a Teflon-AF 2400 capillary filled with methanol, ethanol, and 1-propanol, respectively. The same section of capillary tubing was used in all the 632.8-nm loss measurements; however, this section of tubing was not used in either the broadband loss or Raman measurements. The data in each figure were taken from three separate sets of measurements. It is seen in all three figures that optical loss is unusually high in the small segment of fiber between 0.45 and 0.55 m. Specifically, the average values of loss in this region are 5.9, 4.6, and 3.8 dB/m for methanol, ethanol, and 1-propanol, respectively. By compari-

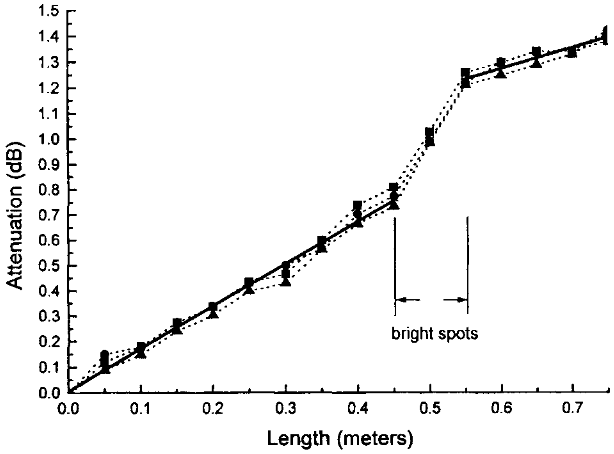

Fig. 3. Attenuation versus length in a Teflon-AF 2400 capillary filled with ethanol (three sets of measurements). Solid lines show the least-squares fit to data between 0–0.45 and 0.55–0.75 m and indicate losses of 1.7 and 0.8 dB/m, respectively, in these regions.

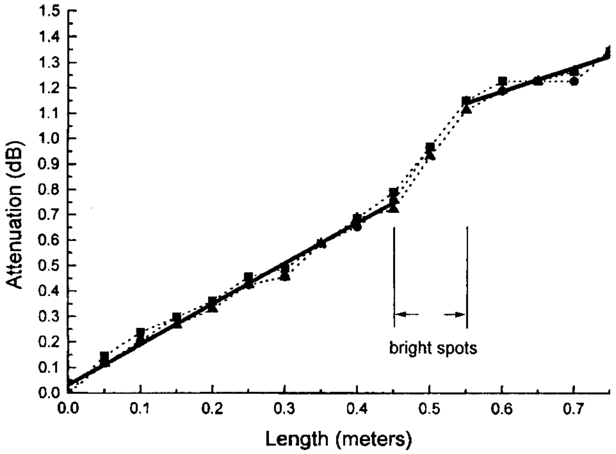

Fig. 4. Attenuation versus length in a Teflon-AF 2400 capillary filled with 1-propanol (three sets of measurements). Solid lines show the least-squares fit to data between 0–0.45 and 0.55–0.75 m and indicate losses of 1.6 and 0.9 dB/m, respectively, in these regions.

son, the average loss values for the same liquids are 1.9, 1.7, and 1.6 dB/m between 0 and 0.45 m, and 1.4, 0.8, and 0.9 dB/m between 0.55 and 0.75 m. These high-loss values, coupled with visual observation of bright spots in the region between 0.45 and 0.55 m, indicate that the increased loss is caused by scattering from imperfections present in this region. The differences in loss observed between the initial 0.45 and the final 0.2 m of the liquid-core fiber may be related to more subtle variations in capillary quality.

A Raman spectrum of acetonitrile ($n = 1.34$) in a Teflon-AF 2400 capillary, acquired in forward-scattering geometry with 350 μW of 514.5-nm radiation, is shown in Fig. 5. For comparison, a spectrum of acetonitrile acquired in backscattering geometry with a conventional spinning sample cell with 100 mW of 514.5-nm radiation is shown in Fig. 6. It is seen that the liquid-core fiber significantly enhances Raman intensity relative to the conventional sampling apparatus. Further, it is seen that with the exception of the broad low-wave-number silica bands[41] generated in the optical fibers used to carry light to and from the capillary, the two spectra are very similar in appearance. Most significantly, neither Teflon-AF Raman bands (which consist primarily of a series of sharp lines between 100 and 850 cm^{-1}) nor additional background fluorescence was observed. A graph of Raman intensity at the 2253-cm^{-1} CN stretch as a function of the effective length of the liquid-core fiber (distance between the input and the output optical fibers) is shown in Fig. 7. Raman intensity in the forward-scattering geometry has been predicted by Walrafen and Stone[10] to vary according to

$$I_R = Kx \exp(-\alpha x),$$

where I_R is the Raman intensity; K is proportional to the product of the intensity of the excitation radiation, the Raman-scattering cross section of the ob-

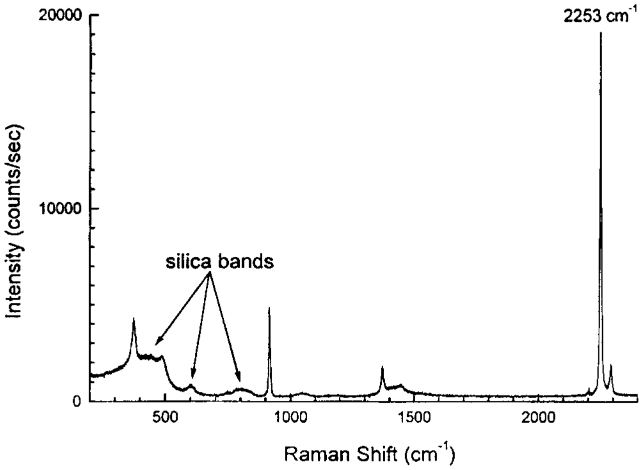

Fig. 5. Forward-scattered Raman spectrum of acetonitrile in a 250-μm i.d. Teflon AF 2400 capillary acquired with 350 μm of 514.5-nm input radiation.

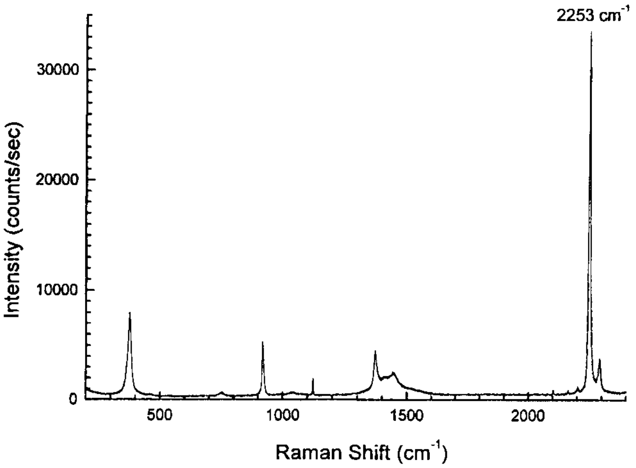

Fig. 6. Raman spectrum of acetonitrile in a conventional sampling arrangement acquired with 100 mW of 514.5-nm input radiation.

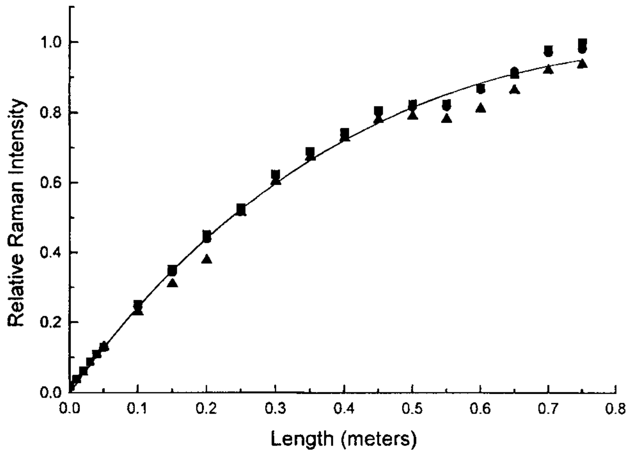

Fig. 7. Normalized Raman intensity at 2253 cm^{-1} CN band of acetonitrile versus cell length (three sets of measurements) and best fit to the model of Walrafen and Stone[10] (see text).

served band in the core liquid, and the solid angle of light guided in the core; x is the length of the liquid-core fiber, and α is the attenuation coefficient of the liquid-core fiber, which is assumed to be the same for both laser and Raman-scattered light. A least-squares fit to this function, in which K and α were allowed to vary, is also shown in Fig. 7. The functional dependence of the data agrees well with the model of Walrafen and Stone,[10] the calculated attenuation coefficient being 4.39 dB/m. The relatively high value of the attenuation coefficient may indicate that the section of capillary used in this work had a somewhat greater number of imperfections than those used in the broadband and the 632.8-nm loss measurements.

4. Conclusions

We have fabricated capillary tubing of Teflon AF 2400, a clear amorphous perfluoropolymer having a refractive index of 1.29, and used it to produce liquid-core optical fibers filled with water, methanol, ethanol, and acetonitrile. We have shown that random long (~0.5–1-m) sections of 250-μm-i.d. fiber can transmit light with losses below 3 dB/m when filled with water and below 2 dB/m when filled with methanol over much of the visible region. However, loss characteristics varied somewhat between different sections of capillary. This variation was attributed, at least in part, to random imperfections in the capillary wall. Shorter sections of capillary with fewer apparent imperfections exhibited losses as low as 0.8–1.9 dB/m at 632.8 nm when filled with alcohols even though OH overtone absorption also contributes to loss at this wavelength. We believe that liquid-core Teflon-AF fibers offer significant benefit in diverse spectroscopic applications and have shown that even fibers with relatively high loss are capable of significantly enhancing the intensity of Raman spectra relative to more conventional sampling arrangements.

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