

Raman lasing near 650 nm from pure water microdroplets on a superhydrophobic surface

A. Kiraz^{*}, S.Ç. Yorulmaz, M. Yorulmaz, A. Sennaroglu^{*}

Department of Physics, Koç University, Rumelifeneri, Sariyer, 34450 Istanbul, Turkey

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Abstract

We demonstrate Raman lasing near 650 nm in pure water microdroplets located on a superhydrophobic surface. In the experiments, stationary, pure water microdroplets were prepared on a superhydrophobic surface and excited by a pulsed, frequency-doubled Nd:YAG laser at 532 nm. Intense laser emission was observed at frequencies corresponding to the whispering gallery mode resonances of the water microdroplets near 650 nm where Raman resonances due to OH-stretching bonds of water are located. On-off behavior was observed during lasing and the average temporal inter-burst separation was determined from the time-dependent intensity traces. Our results can find applications in the development of novel organic light emitters for short-haul communication systems, and in the spectroscopic characterization of water microdroplets on a surface.

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Whispering gallery mode resonators are attractive in developing low threshold Raman lasers due to their high mode quality factors and relatively small mode volumes. Raman lasing has been demonstrated in previous studies using solid microsphere [1], microtoroid [2], or microdisk [3] structures. Liquid microdroplets are alternative whispering gallery mode resonators that can be especially important for developing novel organic light emitting devices suitable for low cost short-haul communication systems. These systems require light sources emitting at around 650 nm due to the low absorption of the plastic fibers [4].

Microdroplet Raman lasers can prove to be important in these applications, because of the fact that they are not fundamentally limited by photobleaching despite being organic light emitters.

Recently, we have demonstrated Raman lasing near 630 nm in glycerol/water microdroplets standing on a superhydrophobic surface [5]. These experiments were performed under ambient humidity conditions ($\sim 45\%$ relative water humidity) where the volume ratio of glycerol in the microdroplets was larger than 80%. As a result, Raman lasing was observed in the Raman bands of Glycerol (in the CH-stretching region near 2900 cm^{-1} [6]) which provide a higher Raman gain than that for pure water [5]. Here, we report Raman lasing near 650 nm (in the region between 2900 and 3700 cm^{-1} where Raman resonances due to OH-stretching bonds are located [7]) in pure water microdroplets standing on a superhydrophobic surface

^{*} Corresponding authors. Tel: +90 212 3381701; fax: +90 212 3381559.

E-mail addresses: akiraz@ku.edu.tr (A. Kiraz), asennar@ku.edu.tr (A. Sennaroglu).

pumped with a pulsed 532 nm laser. Different from the glycerol/water studies, the pure water microdroplets were kept inside a humidity chamber to prevent their rapid evaporation. We note that in previous studies, stimulated Raman scattering has been observed in the OH-stretching modes of liquid water microdroplets near 3400 cm^{-1} [8,9] as well as in other modes located in the range from 2100 to 5100 cm^{-1} [10]. These earlier experiments were performed using a stream of microdroplets generated by a vibrating-orifice aerosol generator. Raman spectra were recorded upon the excitation of a microdroplet by a single high-energy laser pulse. Different from these studies, in this work, we investigate isolated pure water microdroplets on a superhydrophobic surface and the employed experimental configuration allows for recording Raman spectra of the microdroplets upon their excitation by many high-energy laser pulses. As a result, intense Raman emission can be observed from one dominant WGM with a high contrast ratio (signal to noise ratio up to 25 dB), providing strong indication of Raman lasing. To the best of our knowledge, such spectra with only one dominant WGM have not been reported to date using pure water microdroplets.

Superhydrophobic surfaces were prepared by spin coating 60 mg/ml ethanol dispersion of hydrophobically coated silica nanoparticles (Evonik, Aerioxide LE1) on a cover glass. The average contact angle of water droplets of $\sim 2\text{ mm}$ diameter on the superhydrophobic surface was measured to be larger than 150° . An ultrasonic nebulizer was used to spray water microdroplets with diameters ranging from a few up to $\sim 100\text{ }\mu\text{m}$ on to the superhydrophobic surface. A mini humidity chamber was placed on top of the surface immediately after microdroplet generation, preventing evaporation of microdroplets in the absence of pump laser. With the application of pump laser, slight evaporation ($<15\%$ change in radius over one minute of pumping) was observed on individual microdroplets. The diameters reported in this letter correspond to initial values before the application of the pump laser.

The water microdroplets were excited by a pulsed, frequency-doubled Nd:YAG laser at 532 nm (repetition rate = 1 kHz, pulsewidth = 100 ns, average output power = 60 mW) which was reflected off a dichroic mirror and focused to an estimated $25\text{-}\mu\text{m}$ -diameter spot using a microscope objective ($\text{NA} = 0.80$, $60\times$) in inverted geometry. The same microscope objective was used to collect the Raman signal from individual microdroplets. Raman spectra were recorded with a 0.5-m monochromator and a CCD camera (spectral resolution: 0.17 nm). Exposure time of the CCD camera

was 30 s in the spectrum reported in Fig. 1, and 0.5 s in the spectra reported in Figs. 2(a and b) and 3. During consecutive acquisitions the exposure time was followed with 2.2 s readout time. Movies of microdroplets exhibiting Raman lasing were recorded using a band pass filter and a monochrome CCD camera.

Fig. 1 shows the Raman spectrum of the OH-stretching bonds of liquid water located between 2900 and 3700 cm^{-1} . Raman lasing was routinely observed from individual WGMs within this Raman gain region. Spectra obtained from a $13\text{-}\mu\text{m}$ -diameter water microdroplet exhibiting Raman lasing are shown in Figs. 2(a and b) and 3. Consecutive spectra in Fig. 2(a and b) show the momentary observation of intense WGM emission which is a clear indication of Raman lasing. Fig. 2(a and b) corresponds to Raman spectra obtained during the acquisition numbers 5 and 6 in Fig. 3, respectively. Raman lasing was not sustained due to thermally induced density fluctuations, as reported previously for glycerol–water microdroplets [5]. When lasing ceased, intensity of the lasing WGM dropped by more than 25 dB in consecutive acquisitions shown in Fig. 2(a and b). The observation of a single, dominant WGM in Fig. 2(b) is another indication of Raman lasing. For the case of cavity enhanced Raman scattering, all the WGMs within the Raman band of water are expected to be present in the spectrum shown in Fig. 1 (see, for example Ref. [5]). Simultaneous lasing at two different WGMs belonging to different mode sets has also been observed as shown in acquisition number 10 of Fig. 3. We did not attempt to exactly identify the WGMs observed in Figs. 2(b) and

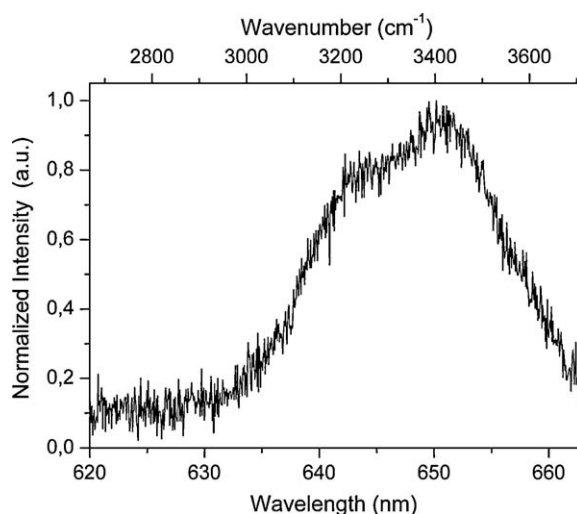


Fig. 1. Raman spectrum of liquid water recorded at room temperature and pressure. The band includes resonances due to OH-stretching bonds between 2900 and 3700 cm^{-1} as discussed in Ref [7].

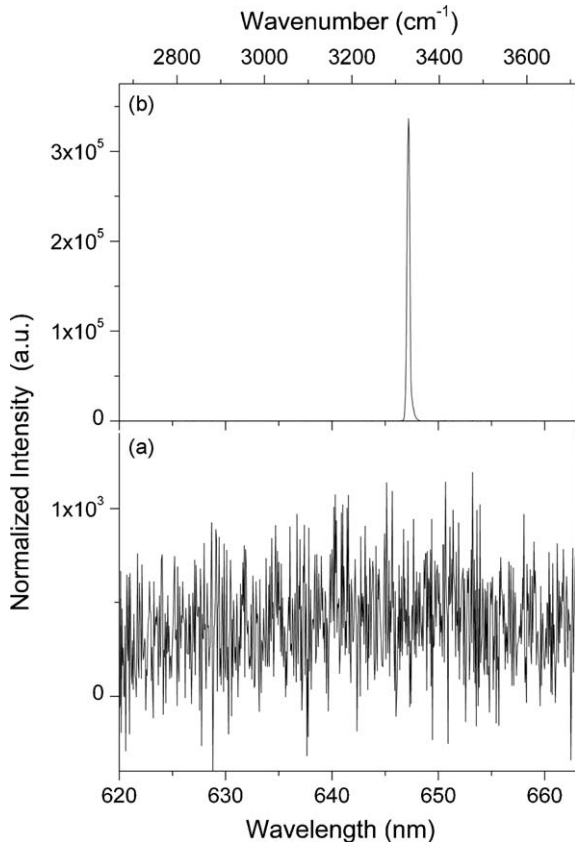


Fig. 2. Consecutive spectra recorded from a 13- μm -diameter water microdroplet during the (a) “off” and (b) “on” periods of Raman lasing. Intensity of the lasing WGM increases by more than 25 dB in consecutive acquisitions.

3 due to evaporation during the experiments, and the absence of the complete set of WGMs within the Raman gain region, such as those seen in the stimulated Raman scattering spectra [8–10]. Considering the peak laser intensity used in our experiments ($\sim 10^8 \text{ W/cm}^2$) together with the Raman gain coefficient of water at 532 nm (0.14 cm/GW), we estimate the quality factors of the WGMs exhibiting Raman lasing to be $\sim 5 \times 10^6$ [11]. This is in agreement with the expected quality factors which can be as high as $\sim 10^8$ for a 10 μm diameter water microdroplet at 532 nm [12].

The time trace of a 14- μm -diameter water microdroplet exhibiting Raman lasing is plotted in Fig. 4. This time trace was generated by analyzing the video of the Raman signal collected from the microdroplet (recorded at a rate of 25 frames/s). The average inter-burst separation in Fig. 4 was 1.2 s, significantly longer than 0.4 s that was observed with glycerol–water microdroplets using nitrogen purging [5]. In the present setup, nitrogen purging was not possible since the

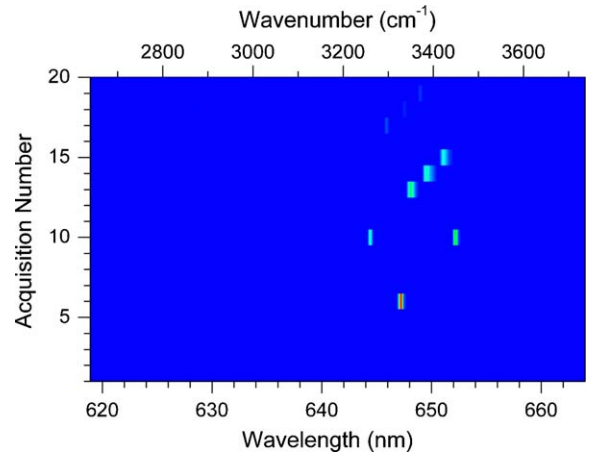


Fig. 3. Contour plot shows consecutive spectra taken from a 13- μm -diameter microdroplet exhibiting Raman lasing. Intensity values in arbitrary units increase from blue to red. Momentary single-mode (acquisition numbers 6, 13, 14 and 15) and multi-mode (acquisition number 10) Raman lasing is observed (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

microdroplets were enclosed inside a humidity chamber and we believe that the longer inter-burst separation suggests slower rate of cooling of the microdroplets. In the inset of Fig. 4, Raman lasing image appears in the form of a ring. The absence of an emissive plume suggests that aerosol-induced laser breakdown is not observed in our case. This is further supported by the fact that the peak laser intensity used in our experiments ($\sim 10^8 \text{ W/cm}^2$) is approximately ten times smaller than

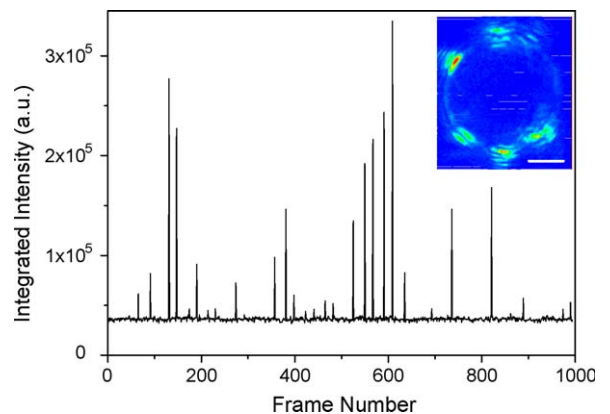


Fig. 4. Recorded time trace of the Raman lasing intensity from a 14- μm -diameter microdroplet shows the “on/off” behavior. The recording rate is 25 frames/s. Average inter-burst separation was observed to be 1.2 s for this microdroplet. Inset shows the image used in calculating the time trace at frame 608. Scale bar shows 5 μm . Intensity values in arbitrary units increase from blue to red (for interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

the aerosol-induced laser breakdown threshold (2–3 GW/cm²) for water droplets at 532 nm laser wavelength [13].

In conclusion, we have demonstrated Raman lasing near 650 nm in 13–14 μm diameter water microdroplets pumped with a pulsed, frequency-doubled Nd:YAG laser at 532 nm. Intensity of the lasing WGMs was not sustained due to excessive heating during Raman lasing. At the end of an “off” period when excess heating was dissipated, Raman lasing was observed to resume. Our results can find applications in the development of novel organic light emitters for short-haul communication systems and in the spectroscopic characterization of water microdroplets on a surface. Furthermore, similar methods may pave the way for the observation of natural lasing in atmospheric aerosols excited by an intense natural pump source such as lightning.

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