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Infrared laser wavelength dependence of particles ablated from glycerol

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ABSTRACT

Particles were generated from glycerol that was irradiated at atmospheric pressure using a mid-infrared optical parametric oscillator at wavelengths between 2.6 and 3.8 μm. The size distribution and quantity of ejected particles with diameters larger than 300 nm were measured using an aerodynamic particle sizer. At a given fluence, the particle concentration roughly tracked the infrared absorption spectrum of liquid glycerol. The threshold fluence for particle formation varied between 1000 and 5000 J/m^2 throughout the measured wavelength range and the minimum fluence corresponds to the IR absorption maxima of glycerol. The mean particle size roughly tracks the inverse of the IR absorption and smaller particles are observed at the greatest IR absorption. The material ejection mechanism is interpreted as an explosive boiling process in the stress confinement regime.

1. Introduction

The removal of material as particulate by laser ablation of solids and liquids has important applications in surgery [1], micromachining [2–4], thin-film generation [5,6], synthesis of nanoparticles [6,7], and chemical analysis [8–19]. The methods using pulsed lasers to remove material for chemical analysis include laser ablation inductively coupled plasma atomic emission spectroscopy (ICP-AES) [8,9], laser ablation inductively coupled plasma mass spectrometry (ICP-MS) [11–13], laser induced breakdown spectroscopy (LIBS) [15–17], and laser desorption ionization mass spectrometry [18], such as matrix-assisted laser desorption ionization (MALDI) mass spectrometry [19]. The formation of particles is the goal of the ICP-based methods; particulate is not detected in LIBS and MALDI, but nonetheless can play an important role.

MALDI, LA-ICP and LIBS can be distinguished by the laser energy regimes used [12]. The lowest energies are used in MALDI and correspond to approximately 10 J/m^2 fluence for lasers operating in the ultraviolet (UV) region. Typical fluences for LA-ICP are on the order of 10 kJ/m^2 and for LIBS the value is MJ/m^2. Laser parameters in the ablation process, such as wavelength, fluence, and pulse width, as well as physical properties of ablated materials, determine the size and quantity of the ejected particles. Molecular modeling studies predict that smaller particles are formed by condensation in the expanding plume of material and relatively larger ones by the ejection of melted material or photomechanical sputtering [20,21]. Owing to the limited size range of the model system, small particles are tens of nanometers or less whereas large particles are those approaching 100 nm in size.

Several studies have been undertaken with the goal of understanding the role of ablation and particle formation in the mass spectrometry technique of matrix-assisted laser desorption ionization. In one study, particles were formed by UV laser ablation and characterized by atomic force microscopy [22]. It was found that the relative quantity of material ejected as molecules compared to particles is strongly dependent on the laser fluence. In another study, a differential mobility particle sizer was used to detect particles below 1 μm created by UV laser irradiation of solid samples containing a MALDI matrix [23]. Two size distributions were observed: one at 10 nm and a second at 100–200 nm. The former is interpreted as resulting from nucleation and condensation and, for the latter, coagulation. In our laboratory, a light scattering particle sizer was used to measure particles larger than 500 nm removed from a MALDI matrix using a 337 nm pulsed laser [24]. Particles with a mean diameter of 680 nm were observed at a laser fluence of 500 J/m^2. The quantity of material removed was close to that found using other methods for the total material removed from a sample under MALDI conditions.

It is known that IR lasers remove significantly greater quantities of material under MALDI conditions compared to UV lasers [25]. In another study from our laboratory, a wavelength-tunable infrared optical parametric oscillator was used to irradiate thin films of glycerol at atmospheric pressure at a limited wavelength range

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between 2.95 and 3.1 μm [26]. Glycerol particles ablated from the sample were detected in a light scattering particle sizer. The threshold for particle formation was 2000–3000 J/m^2 and increased in approximately a linear fashion with laser fluence. The mean particle diameter ranged between 900 and 1600 nm. Although the accessible wavelength range was limited, there were hints that the diameter of the ablated particles tracked the IR absorption of the glycerol. At 3.0 μm, where glycerol has a strong IR absorption due to the OH stretch vibration, the observed particles were the smallest with a mean diameter of 900 nm. At 0.1 μm higher or lower wavelength, the mean particle diameter was about 20% larger. These results are consistent with an explosive phase transition in the stress confinement regime, in which the laser energy is deposited more rapidly than it can be removed through collective molecular motion (acoustic waves) [20,21,27,28].

Photoacoustic waves in glycerol films can be measured using a piezoelectric detector [29]. Ablation of material with 5 ns laser is found to be in the stress confinement regime, whereas ablation with a 100 ns laser is in the thermal confinement regime. High speed photography of the ablation plume shows lift-off of the entire irradiated layer under stress confinement conditions compared to a less dense plume of material created under thermal confinement conditions [30].

In this article, we have extended the wavelength range for the measurement of size distributions of coarse particles ablated from glycerol using a broadly tunable OPO laser system at atmospheric pressure. With this laser system, we were able to tune completely off of the OH stretch absorption as well as access the CH stretch region. Through the change in wavelength, conditions of stress or thermal confinement can be selected. Glycerol was irradiated with a pulsed IR laser with wavelengths between 2.6 and 3.8 μm, covering the absorption band of the OH and CH stretch vibrations. The laser fluence ranged from 1000 to 6000 J/m^2. After irradiation of the target, the particle count and size distribution of ablated material were recorded. The effects of the laser fluence on the ablated particle size and concentration were investigated.

2. Experimental

The particle ablation instrument consists of a commercial aerodynamic particle sizer (Model 3321, TSI, Shoreview, MN) and an ablation chamber that has been described previously [24,26]. Particles were produced by laser ablation of glycerol on a stainless steel sample target at the center of a 140 cm^3 chamber that was suffused with filtered compressed air at a flow rate of 5 L/min. A 2 μL deposit of glycerol (99%, Sigma, St. Louis, MO) resulted in a deposit 6 mm in diameter and approximately 1 mm thick. The glycerol was used directly without further purification.

A wavelength-tunable optical parametric oscillator (Mirage 3000B, Continuum, Santa Clara, CA) operating at 2 Hz repetition rate was directed at the target at 90° through a sapphire window. A CaF_2 lens with 254 mm focal length (at 3 μm) focused the IR laser to an elliptical spot on the target. The spot size was recorded by measuring the mark on laser burn paper, varied from 290 μm × 390 μm at 3.8 μm to 350 μm × 460 μm at 2.6 μm. The temporal pulse width of the OPO is 5 ns. The IR laser was attenuated by inserting a combination of uncoated calcium fluoride, zinc selenide, zinc sulfide, silicon, and germanium optical flats into the beam and the energy was measured using a pyroelectric detector.

The ejected particles were directed into the inlet of the aerodynamic particle sizer to measure the concentration and the size distribution of particles that were ablated from the sample target. The particle size measurement was initiated 10 s after the laser was turned on to begin irradiating the sample to assure that a steady supply of particles was being created. Signals were accumulated for 20 s (40 laser shots).

A Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectrometer (Model 1760; PerkinElmer, Norwalk, CT, USA) recorded the IR spectra of a thin film of glycerol at 400 m^{-1} resolution [31]. The beam path was continuously purged with dry nitrogen. A 45° single pass trapezoidal (SPT) ATR silicon plate (dimensions 50 mm × 20 mm × 2 mm, Harrick Scientific Corporation, NY) internal reflection element (IRE) was mounted in a single beam multiple internal reflection (MIR) attachment (Model 9, Foxboro, MA). Background and sample spectra were recorded by averaging 100 scans.

3. Results

Fig. 1 shows the size distribution of particles ablated from glycerol at wavelengths between 2.8 and 3.6 μm in increments of 0.1 μm. The laser fluence was 8000 J/m^2 at a 2 Hz repetition rate. The particle size distribution did not change significantly as a function of laser repetition rate between 0.5 and 10 Hz. The *y*-axis in each plot extends from zero concentration to 150/cm^3. The plots with a multiplicative factor indicate an expansion of scale. For example, the scale in Fig. 1a (2.8 μm wavelength) is expanded by a factor of 2 (to 150/cm^3 full scale) due to the low concentration of particles observed at this wavelength. The height of each vertical bar indicates the concentration of ejected particles measured in the indicated aerodynamic diameter range; the total particle concentration at each wavelength is given in Table 1 and is at its

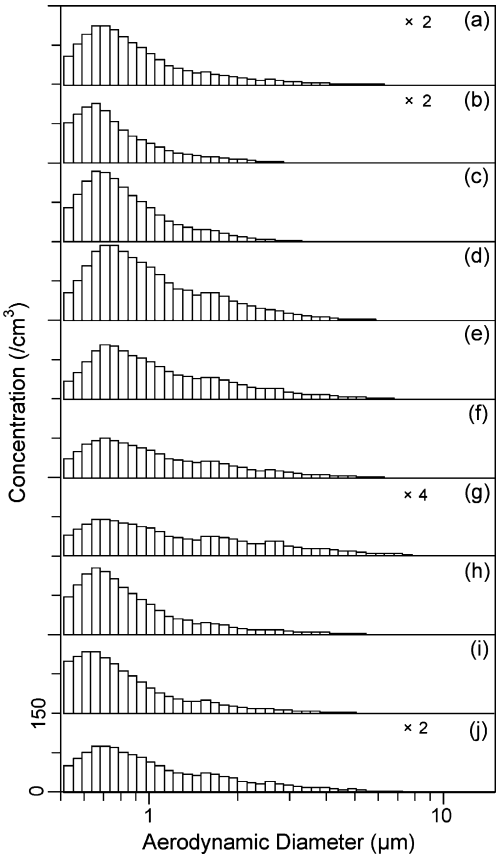

Fig. 1. Particle size distribution measured for irradiation of glycerol at 8.0 kJ/m^2 fluence at different wavelengths: (a) 2.80 μm; (b) 2.90 μm; (c) 2.94 μm; (d) 3.00 μm; (e) 3.10 μm; (f) 3.20 μm; (g) 3.30 μm; (h) 3.40 μm; (i) 3.50 μm; (j) 3.60 μm.