



Long-duration nano-second single pulse lasers for observation of spectra from bulk liquids at high hydrostatic pressures

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ABSTRACT

The influence of laser pulse duration on the spectral emissions observed from bulk ionic solutions has been investigated for hydrostatic pressures between 0.1 and 30 MPa. Transient pressure, shadowgraph imaging and spectroscopic measurements were performed for single pulses of duration 20 and 150 ns. The transient pressure measurements show that for hydrostatic pressures up to 30 MPa, propagation of the high-pressure shockwave generated by the focused laser causes the local pressure to reduce below ambient levels during the time frame that spectroscopic measurements can be made. The pressure impulse and subsequent reduction in pressure are larger, with the latter lasting longer for the 150 ns pulse compared to a 20 ns pulse of the same energy. The 150 ns pulse generates larger cavities with significant enhancement of the spectral emissions observed compared to the 20 ns duration pulse for pressures up to 30 MPa. The results demonstrate that laser-induced breakdown using a long ns duration pulse offers an advantage over conventional, short ns duration pulses for the analysis of bulk ionic solutions at hydrostatic pressures between 0.1 and 30 MPa.

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a form of atomic emission spectroscopy that uses a focused laser pulse to create a plume of excited material that emits light of wavelengths corresponding to the atoms and ions that compose the plume. While most studies concerning underwater LIBS use a double pulse technique [1,2], it has been reported that this method is sensitive to external pressure [3–5], and it has been demonstrated that no enhancement in line emission is observed compared with measurements using a single pulse at pressures of more than 10 and 14.6 MPa for bulk solutions and immersed solids, respectively [3,4]. On the other hand, it has been shown that well resolved emission spectra can be observed at pressures up to 30 MPa after excitation by a single laser pulse of duration <10 ns, with no significant effect of pressure on the analytical value of the line emissions seen for both bulk ionic solutions [6] and immersed solids [7], respectively. In ref. [8] it was suggested that this may be related to the influence of the transient pressure impulse generated when a high power laser pulse is focused in a nearly incompressible medium during the period that spectroscopic measurement is made after a single pulse.

The benefits of long pulse LIBS for underwater spectroscopy were first reported by Sakka et al. [9] who demonstrated an improvement

in the quality of the signal observed from an immersed metallic target by increasing the duration of the pulse used for ablation to 150 ns. It was further demonstrated by the same group that hydrostatic pressures up to 30 MPa have no significant influence on the spectra observed from an immersed metallic target when using a single 150 ns pulse [10]. Here we demonstrate for the first time, that a long-duration pulse is also beneficial for the analysis of bulk ionic solutions at pressures of up to 30 MPa.

The underlying mechanisms of laser-induced breakdown in bulk fluids are well described in literature [11–15]. When a laser pulse of sufficient intensity is focused in a bulk fluid, breakdown can be initiated either through direct ionization of the medium by multiphoton absorption, or cascade ionization at impurities. Once initiated, the energy of the laser is strongly absorbed by the excited plume of material through inverse bremsstrahlung absorption of photons [12]. This rapidly heats the plume to temperatures >5000 K [16], producing visible emissions and local pressures in the order of tens of GPa [12]. The high temperatures and pressures result in rapid expansion of the plume, resulting in high-pressure shockwaves and cavitation effects. As the cavities expand due to the high temperatures and pressures, the pressure inside the cavity reduces to the saturated vapor pressure (2.33 kPa in water at 293 K), which is smaller than the ambient level (0.1 MPa at atmospheric pressure) [17]. The resulting pressure gradient causes the cavity to contract, increasing the pressure inside the cavity until it eventually collapses. While the underlying mechanisms of

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laser-induced breakdown are well documented, the influence of elevated hydrostatic pressures on these mechanisms, and specifically the subsequent effects on the spectral emissions that can be observed from the excited plume are not well understood. In this study, we measure the transient pressure profiles after irradiation of a single pulse in a bulk ionic solution at hydrostatic pressures between 0.1 and 30 MPa. The results demonstrate that the expanding shockwave generated by the focused laser pulse reduces the local pressure near the focal point of the laser to below ambient levels during the period that spectroscopic emissions can be observed for hydrostatic pressures up to 30 MPa. Furthermore, the results of shadowgraph imaging and measurement of the transient pressure profiles show that a 150 ns duration pulse has a stronger influence on the local pressure and produces a larger cavity than a more conventional 20 ns duration pulse of the same energy during the time frame that spectroscopic measurements can be made. While analytically useful information can be obtained for solutions at high-pressure using a conventional single pulse technique [6], it is shown that the use of a long-duration pulse yields significant enhancements in the quality of the spectra observed.

2. Materials and methods

Experiments are performed on bulk ionic solutions that contain 410 ppm Ca and 370 ppm K at pressures of up to 30 MPa using the setup shown in Fig. 1. The concentrations of Ca and K were chosen to match typical values of seawater. The pressure chamber consists of a stainless steel cylinder with three sealed fused silica windows and two electrical penetrators. These allow for simultaneous spectroscopy, transient pressure measurements and shadowgraph imaging of laser-induced plumes at hydrostatic pressures of up to 30 MPa. A modified 1064 nm Nd:YAG Q-switched laser, described previously in ref. [9], is used to deliver a single 25 mJ pulse of 20 or 150 ns duration, where Fig. 2 shows the temporal profiles of the pulses used in this work. These are focused into the bulk solution via a high-pressure objective lens of 10 \times magnification, where the distance between the back of the focusing lens and the focal point of the laser is 9 mm in water. Measurements of the transient pressure profiles are performed using a hydrophone (Müller Instruments Müller-Platte Needle Probe) that is sensitive up to 20 MHz and is placed 1 mm from the focal point of the laser. Dimensionally calibrated shadowgraph images are recorded using an intensified charge coupled device (ICCD) as a detector (Princeton Instruments PiMAX3 1024i Unigen II) together with an objective lens that has a working distance of 46.2 mm in air at 6 \times magnification (Union optics DZ4-T ZC15). A flash lamp is used to back illuminate the shadowgraphs and gated images are taken at various delays from the laser pulse. Spectroscopic measurements are performed by observing the plumes along the same path used for laser delivery.

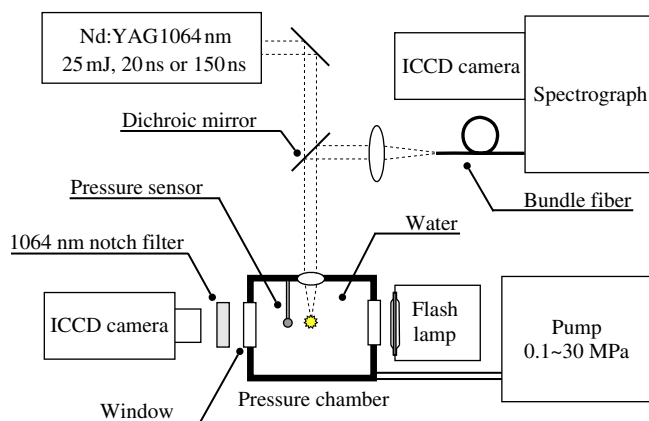


Fig. 1. Experimental setup for investigation of plumes generated in bulk ionic solutions at pressures of up to 30 MPa.

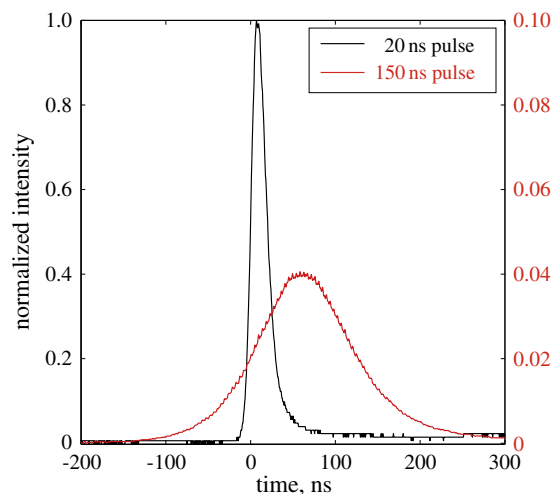


Fig. 2. Measured shape and duration of pulses used in this work. The vertical axis on the left shows the peak normalized intensity of the 20 ns pulse, and the axis on the right shows the corresponding intensity of the 150 ns pulse.

The emitted light is passed through a 150 mm focal length spectrograph with a light throughput of f/4 (Acton Research Spectra Pro 2150), and is recorded using an ICCD (Princeton Instruments PiMAX3 1024i Unigen II). A 1200 groove/mm grating and a 50 μ m wide entrance slit are used during the experiments.

3. Results

Fig. 3 shows the transient pressures recorded over 8 μ s for plumes generated using single 20 and 150 ns duration pulses at 0.1, 10, 20, and 30 MPa, respectively, where time is measured from when the first peak reaches its maximum value. The graphs show the average of 10 profiles measured at each condition. Table 1 summarizes the magnitudes of the first and second peaks, corresponding to the initial laser-induced shockwave and the collapse of the cavity, and the reduction in pressure below ambient levels that occurs between these two peaks. The times at which the minimum pressure between the peaks occurs, and the time of the second peak are included together with the period that the pressure is reduced below ambient levels between the first two peaks. The uncertainty range given is the standard deviation of 10 measurements made at each condition. While it is not possible to determine the absolute magnitudes of the pressures involved, it can be seen that the size of the initial shockwave (1st peak) is $33 \pm 13\%$ larger for the longer duration pulse despite the peak power being significantly lower than for the shorter pulse. For the experiments at high hydrostatic pressures, it can be seen that as the shockwave expands outwards, it leaves behind a region in which the pressure is locally reduced to below the ambient levels of the surroundings. The reduction in pressure is more pronounced at higher pressures, increasing from -3.0 ± 0.4 to -5.7 ± 0.5 mV, and from -3.6 ± 0.1 to -6.2 ± 0.5 mV between 10 and 30 MPa for the 20 and 150 ns pulses, respectively. From the values in the table, it can be determined that the average reduction in pressure for the measurements between 10 and 30 MPa is $17 \pm 7\%$ larger for the 150 ns pulse than the 20 ns pulse. Similarly, the duration that the pressure is reduced to below ambient levels is $23 \pm 10\%$ longer for the 150 ns pulse for hydrostatic pressures between 10 and 30 MPa.

Fig. 4 shows shadowgraph images observed for the different duration laser pulses at pressures of 0.1 and 30 MPa, respectively, where the pulse is focused from the left of each frame. The images are obtained at various delays after laser irradiation, noted in the top right of each frame, and all images are recorded with a gate width of 10 ns. Visible emission occurs immediately following laser irradiation for all conditions. For the 20 ns pulse, several small cavities are generated at different locations along the path of the laser, with expanding spherical

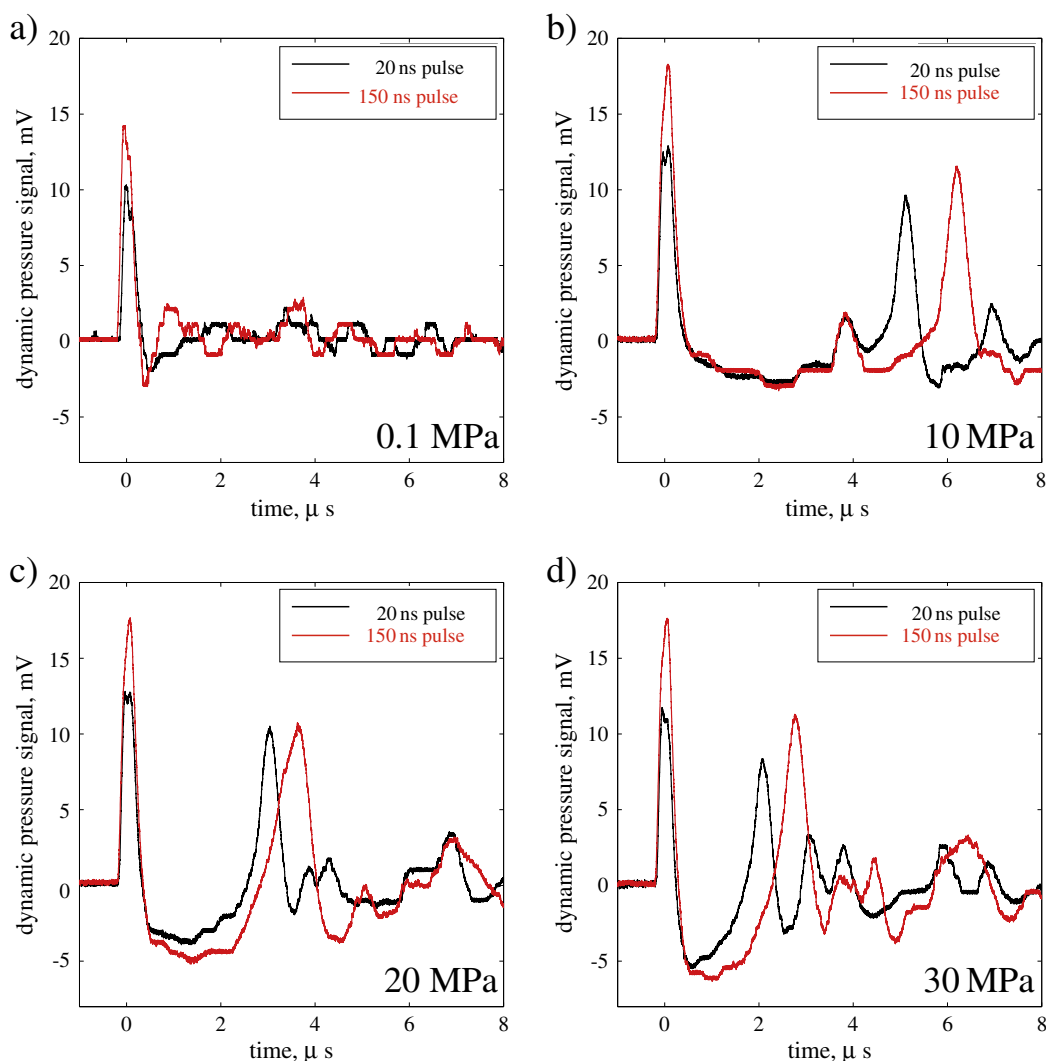


Fig. 3. Transient pressure profiles measured 1 mm from the focal point of single 20 and 150 ns laser pulses in a bulk ionic solution at ambient pressures of (a) 0.1, (b) 10, (c) 20, and (d) 30 MPa.

shockwaves superimposing to form a complicated interference pattern. For the long pulse, the structure of the cavities and shockwaves observed is simpler, with just two merged cavities being formed. Since breakdown occurs when the power intensity is larger than the threshold required to produce free electrons [12], the high intensity near the beam waist of the 20 ns pulse results in breakdown occurring at multiple sites along the focal axis of the laser [13,15]. For the long pulse, breakdown is confined to a smaller region near the focal point of the laser due to the lower intensities. Once the initial free electrons are produced, laser photons are strongly absorbed through inverse bremsstrahlung absorption [10], with cascade ionization occurring at much

lower intensity thresholds. For this reason, the energy of the laser is mostly absorbed by the cavity nearest to the laser [10], as seen in the images where optical emissions are confined to the foremost cavity for both 20 and 150 ns laser pulses at both pressure conditions. The higher transient pressures recorded and more intense optical emissions indicate that the initiated plume absorbs a larger proportion of the laser energy for the 150 ns pulse than the 20 ns pulse. This is in agreement with previous reports that a greater proportion of the laser energy is coupled to the plume for longer pulses due to an increased shielding effect [13,16]. Another noticeable difference is that optical emissions are significantly more intense for the longer duration pulse in the

Table 1

Transient pressure measurements recorded at 0.1, 10, 20, and 30 MPa following irradiation of a single 20 ns and 150 ns pulse. The values shown are the average of 10 measurements and the uncertainty range is the standard deviation of 10 measurements made at each condition.

Hydrostatic pressure	Pulse duration	1st peak	Minimum	Reduced pressure	2nd peak
MPa	ns	mV	mV	μs	mV
0.1	20	12.4 ± 0.6	–	–	–
	150	14.0 ± 0.5	–	–	–
10	20	13.2 ± 0.5	–3.0 ± 0.4	2.3 ± 0.1	8.8 ± 0.5
	150	18.5 ± 0.6	–3.6 ± 0.1	2.4 ± 0.1	10.2 ± 1.0
20	20	13.1 ± 0.7	–4.5 ± 0.4	1.2 ± 0.1	9.1 ± 1.0
	150	18.3 ± 0.8	–5.5 ± 0.3	1.4 ± 0.3	11.4 ± 1.1
30	20	12.2 ± 0.9	–5.7 ± 0.5	0.6 ± 0.1	7.5 ± 0.8
	150	16.7 ± 1.4	–6.2 ± 0.5	1.0 ± 0.3	8.7 ± 2.1

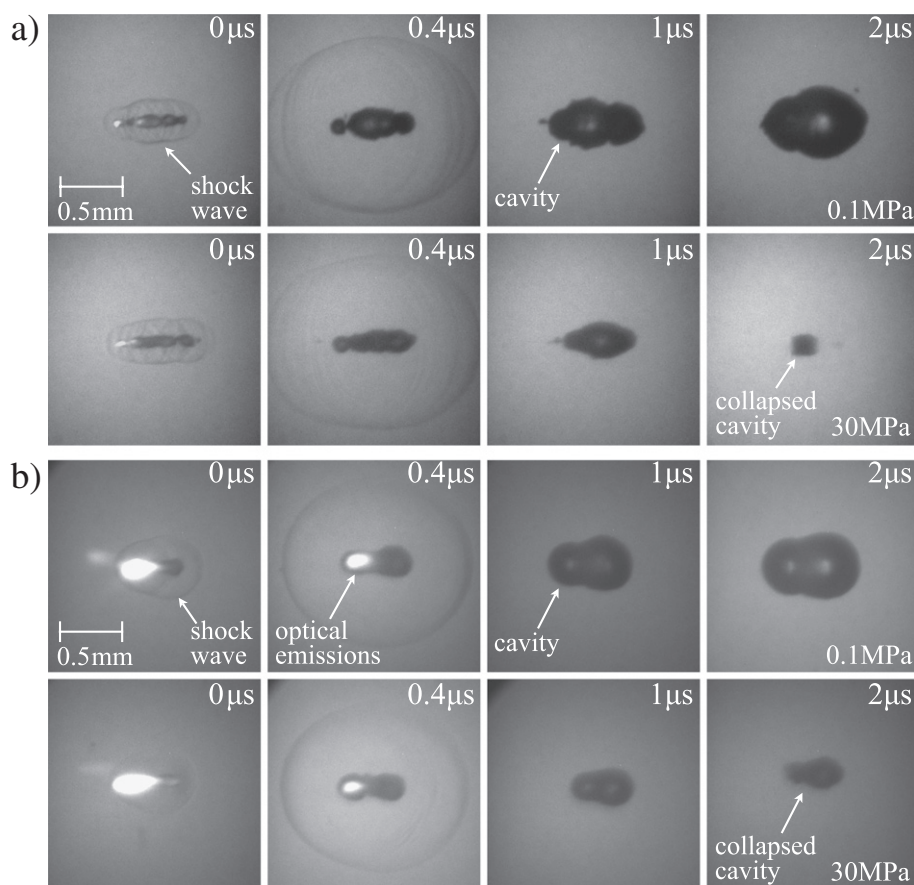


Fig. 4. Shadowgraph images of plumes generated in liquids at 0.1 and 30 MPa (a) using a 20 ns pulse, and (b) using a 150 ns pulse. The number at the top right of each image is the delay from the laser pulse. Each image was taken with a gate width of 10 ns.

images taken at 0.4 μs compared to the corresponding images taken for the 20 ns pulse. The fact that a longer pulse results in a longer period of visible emission is also reported in ref [13], where the luminescence for a 6 ns pulse was reported to last just 15 ns, whereas the optical emissions following a 76 ns pulse lasted for more than 200 ns. At this point, the size of the cavities is similar for both 0.1 and 30 MPa pressure conditions for the respective pulse lengths. However, in the images taken at 1 μs and 2 μs the sizes of the cavities diverge at different pressures. Fig. 5 shows the volumes of the cavities calculated from

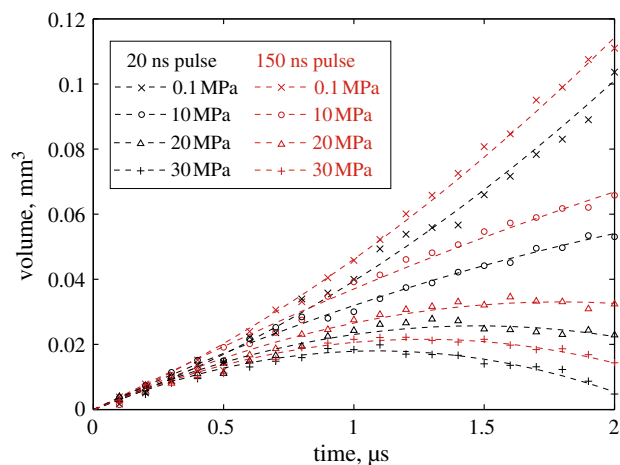


Fig. 5. Volume of cavity generated after irradiation of a 20 and a 150 ns single pulse in a bulk liquid at 0.1, 10, 20 and 30 MPa.

shadowgraph images during the first 2 μs after irradiation with the 20 and 150 ns pulses at 0.1, 10, 20, and 30 MPa, respectively. The volumes are calculated by rotating the cross section of the cavities about the central axis, where in the case of multiple cavities the sum of the volumes is used. The values shown are averaged over 10 measurements for each condition. The dotted line is a spline fit included for clarity of presentation. Even though both pulses have the same total energy, the cavities formed by the long pulse are larger and have longer lifetimes than those formed by the shorter pulse. Although the maximum size of the cavities and their lifetimes are strongly dependent on the hydrostatic pressure of the surrounding fluid [18], it can be seen that the volume of the cavities are similar during the first 0.4 μs after irradiation, indicating that transient pressure impulse due to the focused laser plays a more dominant role in determining characteristics of the cavity than hydrostatic pressures up to 30 MPa during this time frame.

Fig. 6 shows the emission spectra observed for a solution containing 410 ppm Ca and 370 ppm K using a 20 ns pulse (Fig. 6(a, c)) and a 150 ns pulse (Fig. 6(b, d)) at 0.1, 10, 20 and 30 MPa, respectively. The spectra shown are averaged over 10 measurements at each condition. All measurements are performed with a gate delay of 0.4 μs and a gate width of 0.5 μs to allow for comparisons between the measurements. A 0.4 μs gate delay was found to be optimal for both 20 and 150 ns pulses. Measurements made with a smaller delay are affected by the initial continuum due to free-fixed transitions. A longer gate width results in a larger accumulated signal for measurements at low pressure, but is affected by sono-luminescence [19] that occurs when the first cavity collapses at high hydrostatic pressures. A longer gate delay was not used for the same reason. The lines of Ca II at 393 nm $^2P_{3/2} \rightarrow ^2S_{1/2}$, 397 nm $^2P_{1/2} \rightarrow ^2S_{1/2}$, and Ca I at 423 nm $^1P_1 \rightarrow ^1S_0$ can be seen in Fig. 6(a) and (b), and the lines of K I at 766 nm $^2P_{3/2} \rightarrow ^2S_{1/2}$ and

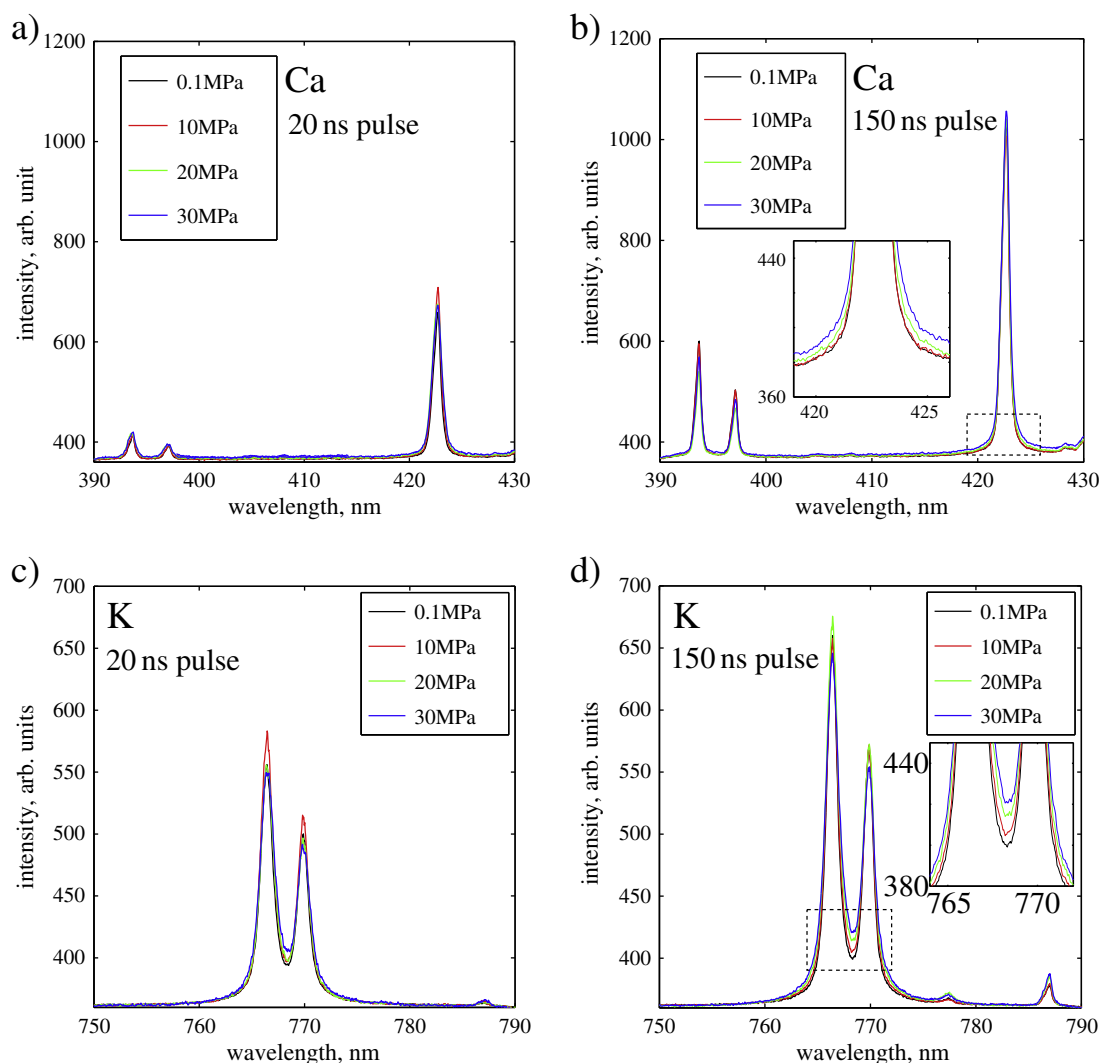


Fig. 6. Spectroscopic measurements of ionic solutions containing 410 ppm Ca measured using (a) a 20 ns pulse, and (b) a 150 ns pulse, and 370 ppm K using (c) a 20 ns pulse, and (d) a 150 ns pulse, at pressures of 0.1, 10, 20, and 30 MPa respectively. A gate delay of 0.4 μ s and a gate width of 0.5 μ s are used for all measurements. Each signal represents the average of 10 measurements performed at each condition.

770 nm $^2P_{1/2} \rightarrow ^2S_{1/2}$ can be seen in Fig. 6(c) and (d). The variation in peak intensity and FWHM with pressure between 0.1 and 30 MPa for Ca I at 423 nm $^1P_1 \rightarrow ^1S_0$ and K I at 766 nm $^2P_{3/2} \rightarrow ^2S_{1/2}$ is shown in Fig. 7(a) and (b), respectively. The peak intensity after subtraction of the background is shown, and the error bars represent the standard deviation of 10 typical measurements under each condition, where all measurements are made using a single shot. The data in red is for the 150 ns pulse, and the data in black is for the 20 ns pulse. It can be seen that there is no significant effect of pressure on the intensity of the signal for both the 20 ns pulse, as reported previously [6], and the 150 ns pulse. The average intensity of the peak obtained using a 150 ns pulse is larger than that obtained using a 20 ns pulse by a factor of $2.2 \times$ and $1.6 \times$ for Ca I at 423 nm and K I at 766 nm, respectively. For Ca I at 423 nm, the FWHM shows some change with pressure, increasing from 0.88 to 1.08 nm for the 20 ns pulse and from 0.84 to 0.89 nm for the 150 ns pulse between pressures of 0.1 and 30 MPa. The FWHM of K I at 766 nm is generally broader than Ca I at 423 nm, and increases slightly with pressure from 1.36 to 1.69 nm for the 20 ns pulse, and 1.19 to 1.39 nm for the 150 ns pulse, between pressures of 0.1 and 30 MPa. Broadening of the peaks can also be seen in the detailed views shown in Fig. 6(b) and (d). In all cases, the FWHM is narrower for the 150 ns pulse. The slight increase in FWHM is attributed to the fact that, although the effects of pressure are small, there is a

slight decrease in the volume of the plumes generated at higher pressure during the period of optical emission, which leads to a higher density of material in the plume. The FWHM for the signals obtained using a long pulse are less sensitive to external pressure, where for Ca I at 423 nm the FWHM is $0.95 \times$ and $0.82 \times$ that observed using a short pulse at 0.1 and 30 MPa, respectively. For K I at 766 nm the relative ratios are $0.87 \times$ and $0.82 \times$ at 0.1 and 30 MPa respectively. For both pulse durations however, the observed pressure broadening effects are of the same order as the measurement error bars, and do not significantly influence the analytical value of the emission lines seen.

4. Discussion

This study has demonstrated that long ns duration laser-induced breakdown spectroscopy is available as a technique to perform spectroscopic analysis of bulk ionic solutions with enhanced spectral characteristics compared to conventional short ns duration measurements for hydrostatic pressures of up to 30 MPa. The enhancement in the intensity of the spectral lines for a 150 ns pulse is in the order of $1.6 \times$ to $2.2 \times$ those measured using a 20 ns pulse for the peaks analyzed in this work. The long pulse also has narrower peaks, with the FWHM in the order of $0.82 \times$ to $0.95 \times$ of those measured using the shorter duration pulse, and while the FWHM increases slightly with external pressure,

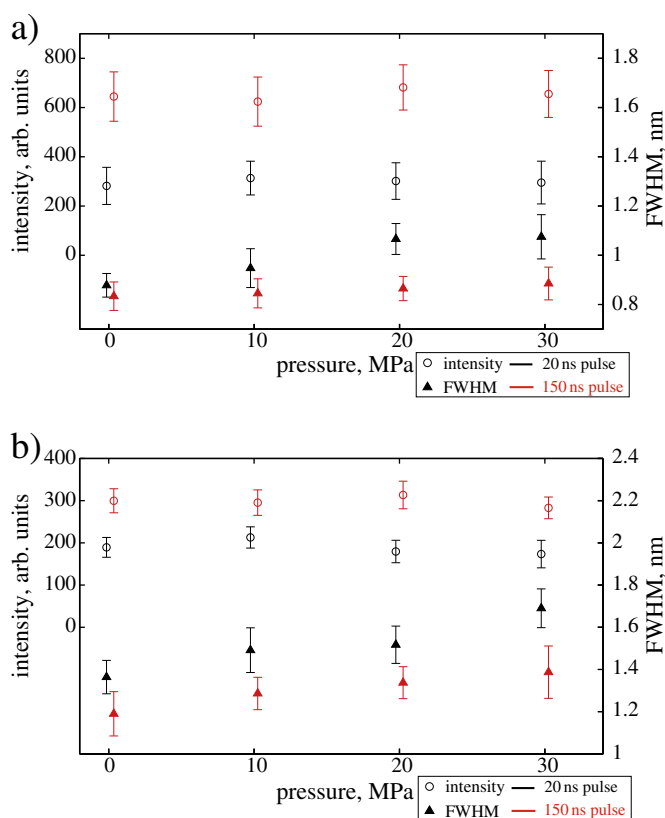


Fig. 7. Variation of peak intensity and FWHM with pressure for Ca I at 423 nm using (a) 20 and 150 ns single pulses, and for K I at 766 nm using (b) 20 and 150 ns single pulse, at pressures of 0.1, 10, 20, and 30 MPa respectively. A gate delay of 0.4 μ s and a gate width of 0.5 μ s are used for all measurements. The graphs show the average and standard deviation of 10 measurements at each condition.

the long pulse is less sensitive for external pressures up to 30 MPa. The enhancement in the intensity of the spectrum is attributed to more efficient coupling of the laser pulse energy into mechanical effects for the 150 ns long pulse, which results in more intense optical emissions compared to a 20 ns duration pulse of the same energy. The results indicate that long-pulse irradiation can improve the quality of spectra observed from bulk ionic solutions at pressures of up to 30 MPa compared to conventional ns duration pulses, and can be used to investigate chemical processes in fluids at supercritical pressures, and perform in situ elemental analysis of fluids in the deep-sea environment.

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