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Title: Multi-Parameter Investigation of Laser Induced Nucleation of Supersaturated Aqueous KCl Solutions

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Abstract:

Various mechanisms have been proposed to explain the non-photochemical laser induced nucleation (NPLIN). Identifying the dominant mechanism requires addressing a large set of experimental parameters with a statistically significant number of samples, forced by the stochastic nature of nucleation.[1] In this study, with aqueous KCl system we focus on the nucleation probability as a function of laser wavelength, laser intensity and sample supersaturation, while the influence of filtration and the laser induced radiation pressure on NPLIN activity is also studied. To account for the nucleation stochasticity 80-100 samples were used. The NPLIN probability showed an increase with increasing laser intensity. The results are different from the previous report, as a supersaturation independent intensity threshold is not observed. No dependence of the NPLIN probability on the laser wavelength (355, 532 and 1064 nm) was observed. Filtration of samples reduced the nucleation probability suggesting a pronounced role of impurities on NPLIN. The magnitude and the propagation velocity of the laser induced radiation pressure were quantified using a pressure sensor under laser intensities ranging from 0.5 to 80 MW/cm2. No correlation was found between the radiation pressure and NPLIN at our unfocussed laser beam intensities ruling out the radiation pressure as a possible cause for nucleation.

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Multi-Parameter Investigation of Laser Induced Nucleation of Supersaturated Aqueous KCl Solutions

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ABSTRACT

Various mechanisms have been proposed to explain the non-photochemical laser induced nucleation (NPLIN). Identifying the dominant mechanism requires addressing a large set of experimental parameters with a statistically significant number of samples, forced by the stochastic nature of nucleation.[1] In this study, with aqueous KCl system we focus on the nucleation probability as a function of laser wavelength, laser intensity and sample supersaturation, while the influence of filtration and the laser induced radiation pressure on

NPLIN activity is also studied. To account for the nucleation stochasticity 80-100 samples were used. The NPLIN probability showed an increase with increasing laser intensity. The results are different from the previous report, as a supersaturation independent intensity threshold is not observed. No dependence of the NPLIN probability on the laser wavelength (355, 532 and 1064 nm) was observed. Filtration of samples reduced the nucleation probability suggesting a pronounced role of impurities on NPLIN. The magnitude and the propagation velocity of the laser induced radiation pressure were quantified using a pressure sensor under laser intensities ranging from 0.5 to 80 MW/cm2. No correlation was found between the radiation pressure and NPLIN at our unfocussed laser beam intensities ruling out the radiation pressure as a possible cause for nucleation.

1. INTRODUCTION

Alternative methods to extend the toolbox for controlling nucleation are sought after. As nucleation is the starting step for the creation of the new crystalline phase, firm control over the nucleation is required to get “first-time-right” crystals. Control of the nucleation rate is required to ensure the formation of a sufficient number of nuclei under optimal conditions for their outgrowth. Moderate supersaturations are used, which maximize the growth while avoiding impurity uptake, the emergence of metastable forms and undesired crystal shapes. Non-Photochemical Laser Induced Nucleation (NPLIN) has been suggested as a promising method to alter the nucleation kinetics. Transparency of supersaturated solutions to the incident light distinguishes NPLIN from the photo-chemically initiated reactions that lead to reactive crystallization. Several reports point out that non-photochemical laser irradiation dramatically reduces the nucleation induction time and controls polymorphism in various fine chemicals relevant for industrial practice.[2-7] Despite the large set of experimental literature on NPLIN, there is no consensus on the working mechanism. Several working mechanisms have been hypothesized so far. The Optical Kerr effect has been first suggested to influence the nucleation due to the density fluctuations resulting from the anisotropic polarization of the pre-nucleation clusters due to electric field of the laser beam[8]. The use of DC fields to control the nucleation of polymorphic forms has supported this hypothesis.[9] On the other hand, simulation of nucleation under the influence of the laser induced electrical field has shown that the field strengths at the laser intensities commonly used in NPLIN studies are too low to influence nucleation.[10] In addition, recent experiments using digital imaging to quantify the orientation of the grown urea crystals with respect to the polarization of the incident laser light during NPLIN did not support the previously claimed influence of laser polarization on the crystal orientation.[11] Laser trapping,[12,13] cavitation,[14-17] formation of bubbles[18,19] and presence of impurities[20] have also been proposed as mechanisms for or aiding NPLIN. Other studies using KCl solutions have explained the observed NPLIN to be due to isotropic electronic polarizability of the KCl clusters.[21] Molecular dynamic simulations carried out on KCl system have also corroborated the existence of electronically polarizable clusters with a relaxation time in the order of 100 ps which is comparable to the laser pulse duration.[22] NPLIN studies using potassium halides (KCl & KBr) showed in general a strong dependence of the nucleation probability on the laser beam intensity, with a probability of 1 being achieved at laser intensities higher than 25 MW/cm2 and no NPLIN effect was observed below 5 MW/cm^2.[23] Furthermore KCl system, required no prior ageing of the supersaturated samples to achieve NPLIN with a single laser pulse and no effect of laser polarization on nucleation was observed.[24] Extensive studies have been carried out to extend the understanding of NPLIN by varying the width of the laser pulse,[25] by limiting the penetration depth of the laser into the sample by use of an evanescent wave[26] and by using micro droplets and gel solutions to gain spatial and temporal control over nucleation[27,28].

Interestingly, recent work has shown the tendency of the supersaturated solutions of various sodium salts and tartaric acid to nucleate under the influence of the laser induced pressure wave (sound/shock wave) passing through the solution.[29] The study claimed that the crystals form as a result of the pressure waves appearing in the sample when the laser is focused into the solution or on the opaque wall of the container containing the solution. The variation of the local pressure and temperature caused by the shock wave was reasoned to alter the chemical potential and hence the nucleation rates. The laser induced shock wave thus adds yet another potential working mechanism for NPLIN.

In this work, we contribute to the current understanding of the NPLIN phenomenon by investigating multiple parameters such as, the laser wavelength & intensity, the supersaturation of the solution and the influence of filtration of the aqueous KCl solution using a statistical significant number of samples. In addition, we have investigated whether the laser induced pressure wave can be correlated to NPLIN. The stochastic nature of nucleation has been taken into account by studying 80-100 samples for quantifying the nucleation probability. The study has been carried out by shining a single pulse of the unfocussed laser beam of different wavelengths (355, 532 and 1064 nm) through aqueous supersaturated solution of KCl. The laser induced pressure has been quantified and its effect on nucleation probability is studied. The radiation pressure caused by the interaction of the unfocussed laser beam with the experimental system (the solution and the glass vial) is quantified by measuring the pressure signal with a piezo-electric transducer placed just below the air-liquid interface. NPLIN was studied with samples at supersaturations (S=1.049&1.027) which were found to be stable to mechanical disturbances and nucleate only when exposed to laser pulse. We showed that a single laser pulse at relatively low beam intensity (~ 0.5 MW/cm2) compared to previous reports[21] can induce nucleation. We discuss our results in depth along with an assessment of potential NPLIN mechanisms.

2. MATERIALS & METHODS

2.1 *Materials and sample preparation*

KCl (≥99%, Sigma Aldrich) and purified water (Elga PURELAB Ultra, Type I+ >18 MΩ.cm) have been used in this study. Solution of KCl in water, with concentration of 369 mg of KCl / g of water and 377 mg of KCl / g of water, was prepared corresponding to a respective supersaturation of 1.027 and 1.049 at 24 °C. The solution was prepared by dissolving KCl in water at 50 °C. 6 ml of heated solution was then transferred into borosilicate glass vials 1.3 cm in diameter and sealed. The vials were again heated overnight in an oven at 50°C to ensure complete dissolution before being taken out and allowed to cool to the room temperature maintained at 24 ±1°C. Therefore, the required supersaturation was maintained with an error of ±2%. In addition, a set of samples were also filtered through a syringe filter (0.45 μm, Whatman Puradisc) when hot as a part of the sample preparation procedure. The syringe filters with cellulose acetate as the filtration media were used which can be autoclaved at 121 °C for setrilzation. The control samples (both filtered and un-filtered) which were brought to the same supersaturation and handled in the same way but not exposed to laser did not nucleate over a period of 1-2 weeks.

2.2 *Experimental Setup and method*

A Q-switched Nd:YAG laser, Continuum Powerlite DLS 8000 model, was used to generate a train of 7 ns linearly polarized light pulses at (the repetition rate of 10 Hz) the fundamental wavelength of 1064 nm. The fundamental beam was further doubled and tripled in frequency via second harmonic generation (SHG) and third harmonic generation (THG) processes in potassium dihydrogenphosphate (KDP) nonlinear crystals to produce wavelengths of 532 nm and 355 nm respectively. The output powers at the new wavelengths could be varied by gently changing the alignment of the KDP crystals and thus altering their SHG/THG conversion efficiencies. The laser beam was then passed through a home-made 2-lens system telescope to shrink beam diameter from 9 mm to 4.5 mm. The energy of the light pulses was measured behind the telescope using a power/energy meter, Gentec Electro Optique- Maestro Monitor, while their duration was precisely monitored with a high-speed photodetector, Thorlabs DET10A 1-ns rise time.

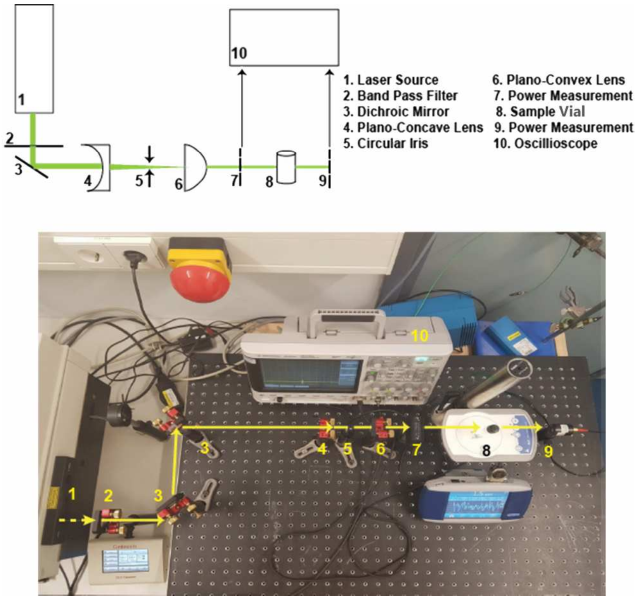

Figure 1. Schematic of the experimental set-up showing different components and path of the laser beam (a) and Photograph of the experimental set-up with the beam path illustrated (b)

To study the NPLIN phenomenon and the resulting nucleation probability, vials were exposed to a single pulse of laser at a particular constant intensity and wavelength. The effect of laser wavelengths on NPLIN was studied at 355, 532, and 1064 nm. For each parameter 80-100 samples were used to ensure a robust set of data. In order to visually detect crystals, a wait period of 60 minutes was observed for each experiment, which was sufficient in all the cases studied in this work (See SI). Precautions were taken to handle the supersaturated sample carefully during experiments to avoid any unwanted mechanical shocks. The number of vials that showed nucleation was recorded and the results were reported as fraction of the total number of vials exposed to the laser pulse, from now on termed as the nucleation probability. The blank samples which were not exposed to the laser pulse were not labile to nucleation for many days at same constant supersaturation.

The interaction of the laser with the sample generates a pressure wave; the pressure fluctuation was quantified in separate set of experiments by dipping a pressure transducer (KISTLER Type 601H with sensitivity of 0.001 bar) just below the air-liquid interface of saturated KCl solution in ultrapure water.

3. RESULTS & DISCUSIONS

Figure 2, shows the nucleation probability as a function of the incident laser intensity at different wavelengths (355, 532 and 1064 nm) for a fixed supersaturation level, S=1.049. The vials exposed crystalized even at low intensities (below 1.5 MW/cm^2). At all the three laser wavelengths used in the study, we report 100% nucleation probability at intensities above of 5 MW/cm^2 (indicating that NPLIN was observed in all the samples exposed to the single pulse of laser within the observation time of 60 min). These results are in conflict with a recent paper, which reported a supersaturation independent threshold intensity (~ 6 MW/cm^2) for NPLIN, in aqueous KCl system using single laser pulses at 1064 nm.[21] The paper reported a very low nucleation probability (~ 10%) with the intensity of approximately 6 MW/cm2. In addition, the nucleation probability of KCl system has been reported to increase linearly with laser intensity in the range of 6-35 MW/cm^2. We see 5 MW/cm^2 to be the saturation intensity above which nucleation probability was 100% while below this intensity value, a decreasing trend in the nucleation probability is seen. It should be noted that the procedure for cleaning the vials and filtering of the solution was different in the reported literature and the present paper. This difference in impurity level has been addressed further in this paper. Our observation is comparable to reports with an aqueous solution of glycine where NPLIN activity has been reported to be a non-linear function of the laser intensity, approaching a saturation value.[3] Based on our observations, the threshold intensity to trigger NPLIN is low, irrespective of the wavelength of the incident laser. The strong dependence of NPLIN on the laser beam intensity can also be speculated to be due to NPLIN mechanisms such as electronic polarizability which theoretically depend on the laser electric field strength.[3] Additionally, the nucleation probabilities are higher with the 355 nm wavelength. To ensure that the role of photochemistry is ruled out at the shorter wavelength of 355 nm, the intensity of the pulse was checked before and after it passed the vial. The variation in the intensity measurements were similar to measurements at wavelength of 532 nm and 1064 nm, confirming the transparency of the solution. Although, with the present results, it is difficult to reason the higher nucleation probability at 355 nm.

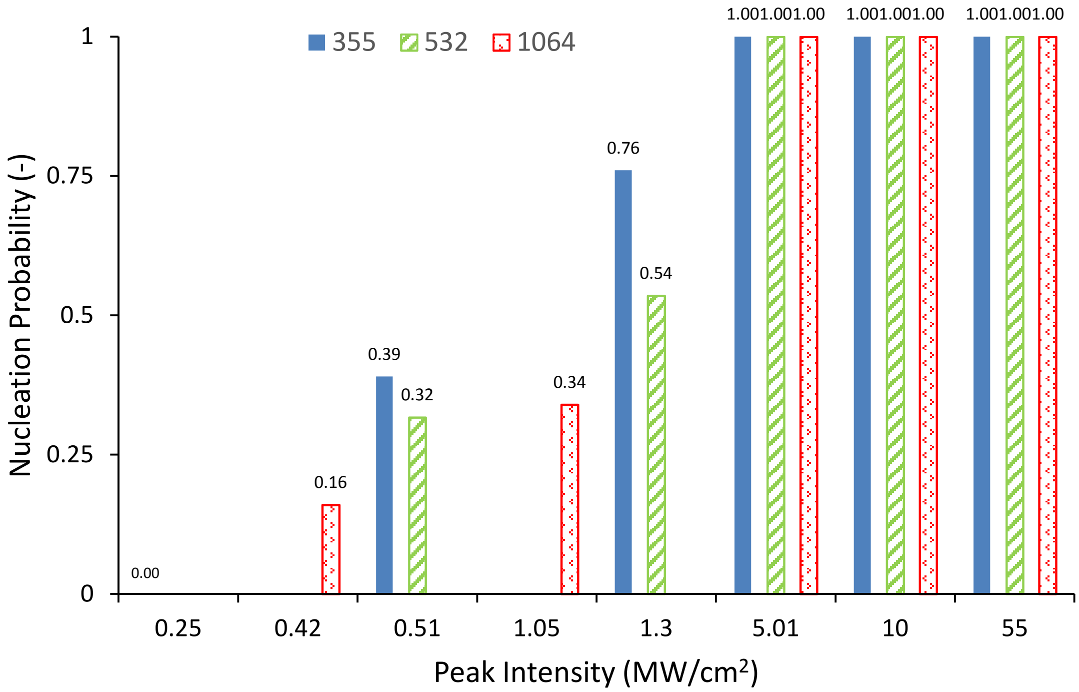

Figure 2: Nucleation probability (the ratio of number of samples nucleated to the number of samples exposed- the commonly used terminology in literature) at 60 mins after laser irradiation as a function of the laser intensity at different wavelengths (355, 532 & 1064 nm) and at a fixed supersaturation (S =1.049). Experiments were done with 80-100 unfiltered samples for each parameter.

The nucleation probability was measured as a function of the laser intensity also at a lower supersaturation (S = 1.027). Figure 3, shows the nucleation probability (at 60 mins after laser irradiation) as a function of laser intensity at 532 nm and at two supersaturations, S = 1.049 & 1.027. As expected, the nucleation probabilities are lower at the lower supersaturation. Unlike the relatively high nucleation probability of the samples at S=1.049 at the two lowest intensities, no NPLIN took place at S=1.027. NPLIN at the higher supersaturation (S=1.049) and low intensities (below 10 MW/cm^2) resulted in only a few crystals (2-4 in number). As per classical nucleation theory, due to the strong non-linear dependence of nucleation rate on supersaturation, the nucleation probability is significantly reduced at the lower supersaturation (S=1.027). However, the growth rates will not drastically differ due to the mostly linear dependence with the supersaturation. Therefore, even if only a few nuclei would have been formed in the experiments with the lower supersaturation, the detection probability would be about equal.

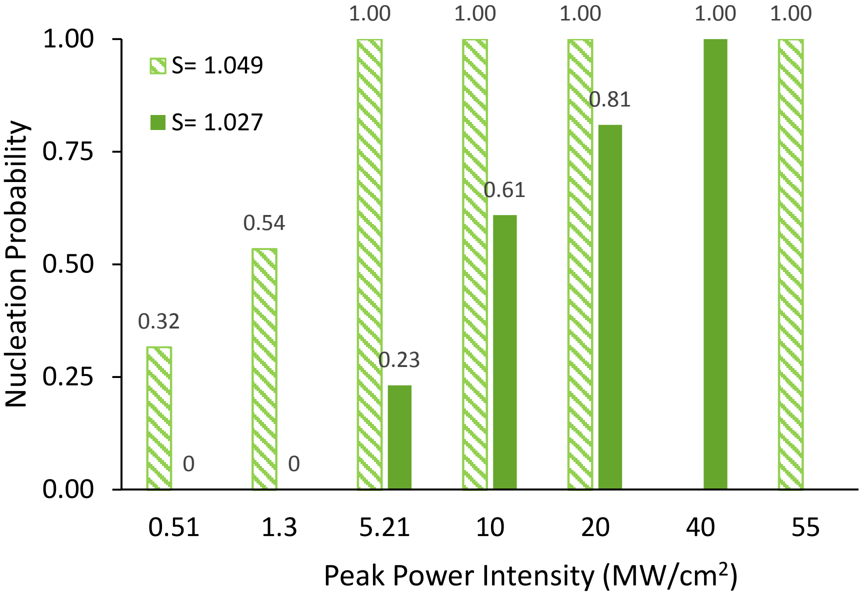

Figure 3: Nucleation probability (at 60 mins after laser irradiation) as a function of the laser intensity at two supersaturations (S = 1.049 & 1.027) and fixed wavelength of 532 nm (based on 100 unfiltered samples).

Our results do not show a supersaturation independent laser intensity threshold as reported in literature. The existence of a supersaturation independent intensity threshold (6 MW/cm^2) was explained to be due to the inability of the weak electric field to bring about isotropic electronic polarization.[21] Thus, our observation showing supersaturation dependent NPLIN threshold (Figure 3) at very low intensities cannot be explained solely based on the proposed isotropic electronic polarizability mechanism.

Interplay of several mechanisms such as optical Kerr effect, susceptibility of samples to mechanical shocks or presence of impurities has been suggested during NPLIN. An explanation to our observation of high nucleation probability at low laser intensities could be the presence of impurities, which have been reported to enhance the NPLIN effect.[20,30] Our results showing a high nucleation probability are based on unfiltered samples. Experiments with samples filtered using a 0.45 μm syringe filter resulted in significantly reduced nucleation probabilities (based on 20 samples at each intensity). Figure 4 shows the difference in the nucleation probabilities between the filtered and unfiltered samples at two wavelengths, 532 and 1064 nm respectively and at a fixed supersaturation of 1.049. Irrespective of the wavelength, the nucleation probability is lowered upon filtration and no NPLIN is observed at intensities below 0.5-1.5 MW/cm^2. Our observation shows that presence of impurities may aid NPLIN which is in agreement with the earlier reported results[30]. In blank experiments, employing unfiltered samples and no laser light, the impurities alone are not able to cause nucleation as none of the supersaturated samples nucleated for days. A possible mechanism could be that the impurities facilitate the laser induced nucleation process by lowering the free energy required to make the solute clusters critical (heterogeneous nucleation). Alternatively, NPLIN could be the direct result of laser-impurity interaction that can cause local heating and the formation of bubbles/cavity which act as nucleation sites[19]. Since filtration reduces the amount of impurities the laser-impurity interaction will also be reduced explaining the reduced nucleation probability.

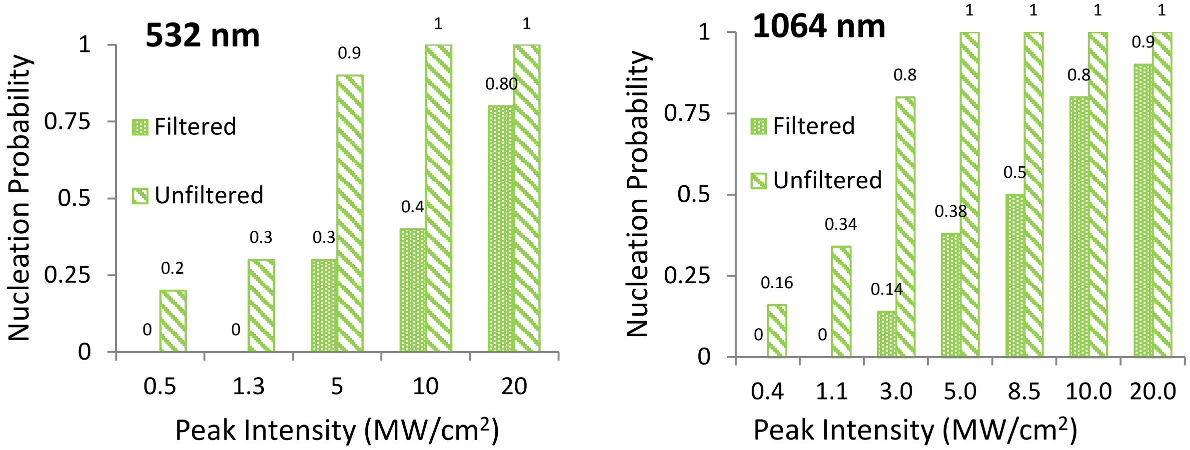

Figure 4: Comparison of nucleation probabilities (at 60 mins after laser irradiation) using 20 each of the filtered and unfiltered samples as a function of the laser intensity at two wavelengths of 532 and 1064 nm and at a fixed supersaturation (S=1.049).

In literature, the presence of impurities larger than 200 nm are not necessary to see the NPLIN phenomenon, as use of clean environment, ultrapure ingredients and rigorous cleaning of the vials did not result in significantly different nucleation probabilities [21]. However unfiltered samples have been reported to be more labile to laser induced nucleation. It is also believed that filtering the solution may reduce the pre-existing subcritical clusters, thereby reducing the nucleation probability. On the other hand addition of nano-particles has been shown to enhance NPLIN.[20] In our case we remove large impurities only (above 0.45 μm) and make sure there is no crystallization during filtration which can reduce supersaturation.

In a recent study, a laser induced pressure wave is identified as an potential mechanism triggering nucleation.[29] The pressure wave generated by the interaction of the laser beam with an opaque surface in contact with the supersaturated solution was able to induce nucleation. The study estimated that a pressure variation in the order of 1 MPa was required to influence the nucleation kinetics. Similarly laser focused directly into the supersaturated solution has also been reported to promote nucleation via a shockwave resulting from collapsing vapor bubble.[14] However these studies were carried out with a focused laser which transfers very high intensity into the solution, about 2 orders of magnitude higher than the unfocused laser beam used in this study and also in conventional NPLIN experiments.

In our study with the unfocused laser beam, a pressure signal was measured after a single pulse of laser passed the sample. Vials containing KCl solution or water were used to measure the pressure signal at a fixed distance from the path of the laser beam through sample vial. Figure 5 shows the peak pressure values as a function of the laser intensity in vials containing aqueous KCl solution. Pressure signal in the 2-20 mbar range is measured at characteristic laser intensities used in our study (0.5 - 80 MW/cm2). At higher laser intensities, the pressure signal is higher. The use of a low energy unfocused laser beam at 532 nm, rules out cavitation (due to absorption of energy) as the solution is transparent to the beam. Even though the laser pulse lasts only for 7 ns, the pressure signal has a decay time of a few milliseconds possibly due to reflections of the acoustic wave within the sample vials (see SI). The pressure signal may originate from the momentum transfer of laser photons to the solution as the refractive index changes along the beam path through air-glass and glass-solution interfaces.[31] Reflections at the glass surface of sample vial also contributes to the generation of the pressure wave. In order to test the effect of the laser induced pressure on nucleation, we prepared two sets of samples filled with identical solutions: one “masked sample” where we blocked the incident laser beam (intensity 80 MW/cm^2) by placing a small piece of black tape on the surface of the vials the other “unmasked” control sample where the laser can pass through and interact with the solution in vials. Figure 6, shows the masked and “control” vials and the resulting nucleation probability

(S=1.049) as well as the measured pressure signals. A much higher pressure signal (around 200 mbar) was measured for the masked samples probably due to the transfer of all the energy onto the tape. As shown in figure 6, no nucleation was observed in the masked vials. 100 samples were tested (also at a lower supersaturation S =1.027) and none of the samples nucleated. Nucleation only occurred in control samples where the laser was allowed to pass through the solution. Our experiments confirm the presence of laser induced pressure wave however it does not contribute to nucleation at laser intensities and supersaturations used in our experiments.

When the laser is absorbed into the sample, for example, in the case of a laser absorbing dye, a high amount of energy is transferred which can result in cavitation generating localized shockwaves[13]. Then the resulting nucleation is probably due to the cavitation. In our study the laser pulse passes through the transparent solution and hence the transferred energy is small hence unable to cause cavitation. Since we observed NPLIN at very low laser intensity (0.5 MW/cm^2) we believe presence of impurities play a role in aiding NPLIN. Moreover, the pressure signals we measure are in the same order of magnitude as the predicted theoretical values of the radiation pressure (see SI) and the magnitude is too low to influence nucleation kinetics.

Our observations are in agreement with the various mechanisms proposed to influence NPLIN. We do not ascertain a single mechanism to be in play during NPLIN, but it is shown that the nucleation is not due to the radiation pressure at laser intensities commonly achieved with an unfocussed laser beam.

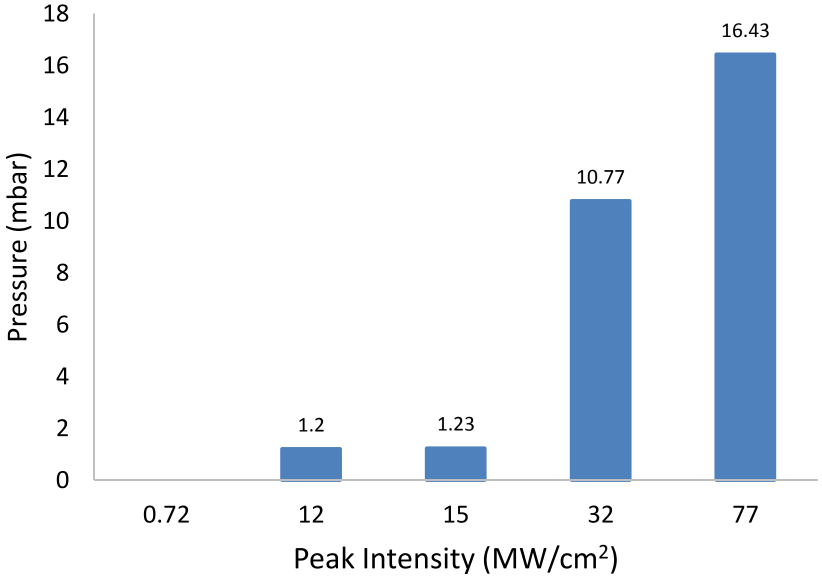

Figure 5: The pressure signal upon irradiation of the vials with unfiltered saturated aqueous KCl solution with a single shot of laser at 532 nm at different laser intensities.

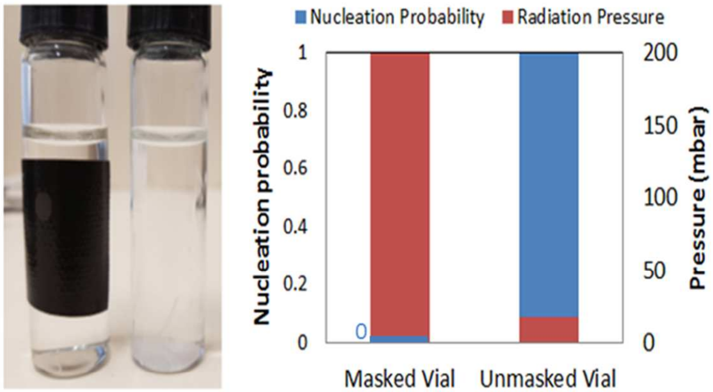

Figure 6: The resulting peak pressure signal and nucleation probability (S=1.049) in the masked and the unmasked vial upon irradiation of a single laser pulse at intensity of 80 MW/cm^2. Despite the higher induced pressure in the masked vial (shown in red in the bar graph), no

nucleation was observed (shown in blue in the bar graph) compared to the “unmasked” control case where laser pulse could pass through.

4. CONCLUSIONS

We focused on the laser induced nucleation phenomenon in aqueous KCl solutions in a multi parameter study spanning laser wavelength, intensity and supersaturation. We also studied the influence of filtration and the correlation between NPLIN activity and laser induced radiation pressure. The NPLIN probability is found to depend on the laser intensity and the supersaturation but independent of the laser wavelength at 355, 532, 1064 nm. In contrast to previous reports, we did not observe a supersaturation independent intensity threshold below which no nucleation is observed. High nucleation probabilities were observed with unfiltered samples; a 100% nucleation probability emerged at laser intensities where in literature low nucleation probability has been reported.[21] Filtering the samples prior to studying NPLIN resulted in lowering of the nucleation probabilities, which highlights the role of submicron impurities in enhancing NPLIN.

We characterized the magnitude of the laser induced pressure wave. Based on our measurements (estimation of the pressure wave velocity shown in SI), the resulting wave is not a shock wave but a sound wave at the laser intensities used in the study. Blocking the laser beam at the surface of the sample vials resulted in larger induced pressure compared to the “unmasked” control case where laser pulse did pass through the sample vials. However, nucleation was completely absent in masked samples. The quantification of the pressure wave intensity and velocity along with the nucleation probability experiments with masked samples enabled us to rule out presence of strong shock wave which can induce crystallization and have been identified as a potential working mechanism for NPLIN. We believe our multi-parameter study will contribute to mechanistic understanding of NPLIN as it examines a single model system evoking all the key experimental parameters with statistically significant repetitions-a commonly critiqued point in NPLIN literature.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The first and the second author have equal contribution to the paper.

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Supporting Information (SI)

The solubility data of KCl in water, cumulative nucleation probability as a function of time and the characterization and measurement of radiation pressure have been elaborated in the SI

ABBREVIATIONS

NPLIN, Non-Photochemical Laser Induced Nucleation.

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Multi-Parameter Investigation of Laser Induced Nucleation of Supersaturated Aqueous KCl Solutions

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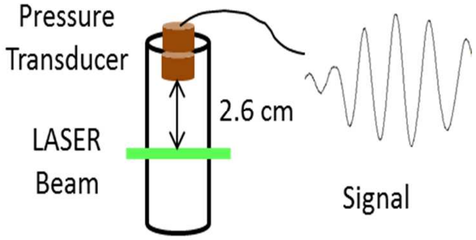
Table of Contents Graphic



Synopsis

Multiple parameters study on NPLIN showing a strong dependence of the nucleation probability on the laser intensity. Weak laser intensities (depending on sample supersaturation), independent of the laser wavelength, were sufficient to trigger NPLIN. Presence of impurities was observed to aid NPLIN and the laser induced radiation pressure resulting from the low energy unfocussed laser pulse did not induce nucleation.