

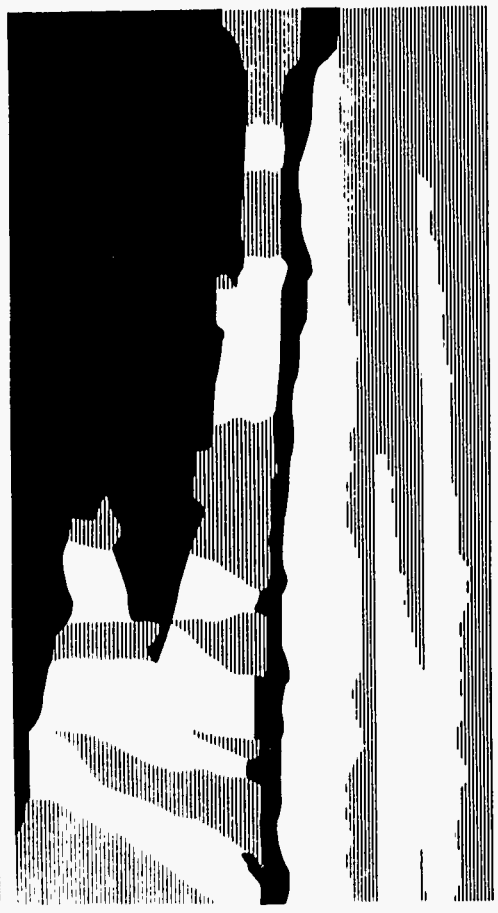
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Title: BUBBLE CHAMBER SPECTROSCOPY FOR CHEMICAL ANALYSIS:
A NEW CONCEPT

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Bubble chamber for chemical analysis: a new concept

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ABSTRACT

A new technique for the detection of trace concentrations of molecules in solution has been developed. This system utilizes the amplification characteristics of a bubble chamber in which energy deposition from laser absorption is monitored. In the experimental set-up, a trace quantity of solute is introduced into liquid propane that is contained in a small (10 ml) stainless steel cell at 120 psi. The propane is superheated by sudden reduction of the cell pressure. Before wall nucleated boiling occurs, target solute molecules are energized by a laser pulse. Absorption of pump laser energy results in the formation of nucleation centers which develop into bubbles and which in turn are detected by CCD camera. Preliminary experiments with crystal violet used as a test absorber have demonstrated detection sensitivity of 10 parts per trillion (ppt).

Keywords: bubble chamber, spectroscopy, trace, superheated, nucleation centers, bubbles, crystal violet

1. BUBBLE CHAMBER SPECTROSCOPY

As a sensitive high energy particle and ionizing radiation detector, the bubble chamber has played an immensely important role in the field of high energy physics.^{1,2} Bubble chambers employ the principle that high energy particles passing through a metastable superheated liquid transfer some part of their energy into the fluid and initiate phase transitions along the particle's trajectory. As pointed out by Seitz and others, the key to bubble formation in these fluids lies in energy deposition intense enough for localized heat transfer to induce a phase transition and create a small "pocket" of gas called a nucleation center.³⁻⁶ Since the surface tension of the surrounding fluid will tend to compress these gas pockets, bubbles can only grow if sufficient energy was absorbed to create enough gas for the internal pressure to overcome the compressive force. Nucleation centers larger than this critical size will grow spontaneously through evaporation of the superheated liquid. If insufficient energy is deposited and the critical size is not met the surface tension will collapse the bubble and the gas will revert to its liquid phase.

A laser beam propagating through such a superheated fluid in a bubble chamber may be expected to demonstrate similar effects. Energy is deposited into the system through absorption excitation. The radiationless relaxation of the excited constituents dissolved or suspended in the superheated liquid induces phase transitions and creates nucleation centers through localized heating. The sudden mechanical release of pressure on the system induces bubble growth from these centers. Preferential boiling from these nucleation centers precedes wall nucleated boiling, making analysis of bubbles in the laser beam path possible. This technique has been demonstrated to be both feasible and trace sensitive.

Conventional absorption spectroscopy techniques such as UV-Vis and IR measure the small intensity losses in a transmitted optical beam. The sensitivity of such techniques is limited due to the difficulty in measuring a small change in a very large signal. A number of new techniques have been developed which avoid this difficulty by measuring the energy deposition in the absorbing medium directly. New photothermal techniques promise increases in sensitivity⁷, but some of these require a chemical reaction to "amplify" the photoacoustic signal.^{8,9} Such reaction based techniques cannot be utilized universally and the chemical reactions themselves may complicate the process. In contrast, the use of a bubble chamber allows detection at extremely sensitive levels (part-per-trillion already demonstrated) utilizing the energy stored in the superheated liquid to "amplify" without the introduction of additional chemical species into the system.

There are several advantages to using a bubble chamber for trace analysis: first, bubble chamber spectroscopy may have the potential for single molecule detection; second, the technique allows sensitive detection for non-fluorescing molecules through absorption; and third, it applies to liquid samples or samples suspended in a liquid media, simplifying sample preparation. Furthermore, this technique is readily interfaced with common separation techniques such as liquid chromatography and supercritical extraction. As an imaging technique bubble chamber spectroscopy may be used to simultaneously image the effects of multiple laser beams such as pump-probe experiments or multi-wavelength experiments.

2. EXPERIMENTAL SETUP

The bubble chamber spectroscopy apparatus is exceptionally simple, consisting solely of the bubble chamber itself, pump laser, image processor and control electronics. The bubble chamber is a small six way stainless steel cube (10 ml interior volume) modified to hold four quartz windows in the vertical faces. The bottom face has a flexible stainless steel bellows compressed by application of pressurized nitrogen (120-160 psi) modulated with a solenoid valve. The cell is filled through piping in the top face, where a piezoelectric pressure transducer is attached (Figure 1).

Bubble growth in the metastable fluid is initiated through release of the bellows pressure by the solenoid valve. Pressure pulse width and amplitude are varied by changes in gas pressure and driving voltage applied to the valve. The pulse shape is monitored by the pressure transducer on the top of the cell. Typical pressure pulses are 1.2 ms FWHM over a 30-40 psi drop. A low duty cycle of 0.2 Hz ensures that the system has time to return to equilibrium before each measurement.

Factory supplied high purity research grade propane (Matheson) is used without further purification as the bulk media in the cell. It has a low absorption cross section in the visible and near-UV and its modest vapor pressure of 110 psi at room temperature allows operation of the cell without the complications of constructing a high pressure cell or operating at low temperature. Additionally, it has a strong enough solvent strength to keep most organic compounds in solution. Before being fed into the cell, the propane is liquefied in a storage container and passed through a series of 0.5 μm stainless steel filters.

The samples themselves are diluted in spectroscopic grade acetone and injected into a 20 μL storage loop. Propane flow into the cell is diverted through the loop and the sample is then flushed into the cell.

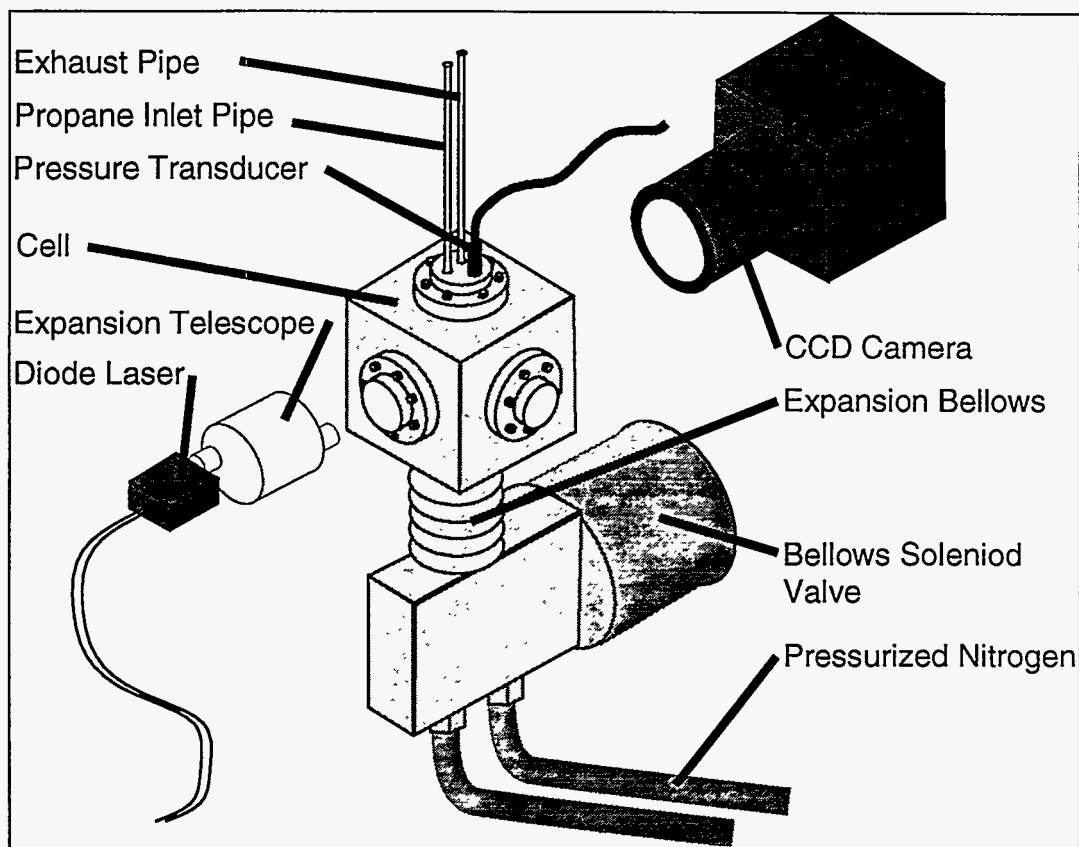


Figure 1. Bubble Chamber Spectroscopy Schematic.

Once a sample is loaded, the cell is allowed to come to thermal equilibrium. The setup is run at room temperature (25° C) without temperature stabilization. Pulsing the solenoid valve allows the bellows to expand under pressure from the propane. Approximately 30 ms after the valve is pulsed and before wall nucleated boiling occurs, the pump laser is passed through the cell. The pump laser is a frequency doubled Nd:Yag (532 nm) with a 10 ns pulse width. This laser pulse is softly focused by a 500 mm lens to a 2 mm beam waist in the cell. Beam energy as measured at the exit window is varied from 30 μ J to 3 mJ. Energy from the pump laser is absorbed by the sample molecules, which transfer the energy into the propane through non-radiative coupling. This energy induces localized heating in the propane and turns the metastable fluid into the gaseous phase at these sites. If these nucleation centers contain enough gas (>critical size) for the internal pressure to overcome the surface tension of the surrounding fluid a bubble will grow at that site. Since the energy for formation of the nucleation center comes from the laser pulse, bubble formation will occur in the laser induced nucleation centers well before wall nucleated boiling occurs. This allows a CCD camera with a macro-lens (100 mm focal length) to take a clear picture of the bubbles in the beam path. The bubbles are back-lit by an expanded and collimated laser diode beam so that the CCD sees them as dark circles with bright centers. Finally the CCD video signal is captured by an asynchronous frame grabber and analyzed with a computer controlled image processing card. Baseline tests show that no bubbles are formed when the pump laser is fired before or after the pressure pulse.

Proof of principle tests were conducted using crystal violet (CV) as a test sample. Crystal violet has a strong absorption in the visible region with a $6.6 \times 10^{-17} \text{ cm}^2$ cross section at 532 nm with a very

small fluorescence quantum yield.¹⁰⁻¹² These characteristics make crystal violet an excellent candidate for initial testing because virtually all photon energy absorbed remains in the system and contributes to the formation of the nucleation center.

3. RESULTS

Although propane has very little absorption at 532 nm, even in the purest grade propane commercially available (Research grade, Matheson) there are still a significant number of bubble forming impurities. The presence of bubbles in the neat propane solution (Figure 2) makes it clear that propane itself produces some baseline bubble count. This baseline count is the limiting factor to the technique's sensitivity. Each frame of data in Figure 2 was taken with a single 210 μ J laser pulse at time delays of 150, 850 and 2300 μ s. Since the bubbles in each frame are of a uniform size and since no bubbles are present outside the laser beam path one may conclude that the bubbles are the result of light absorption initiated single nucleation events in individual molecules or micro particles. Further, as the succession of frames in Figure 2 illustrates, bubbles grow spontaneously in the superheated fluid and eventually move upwards.

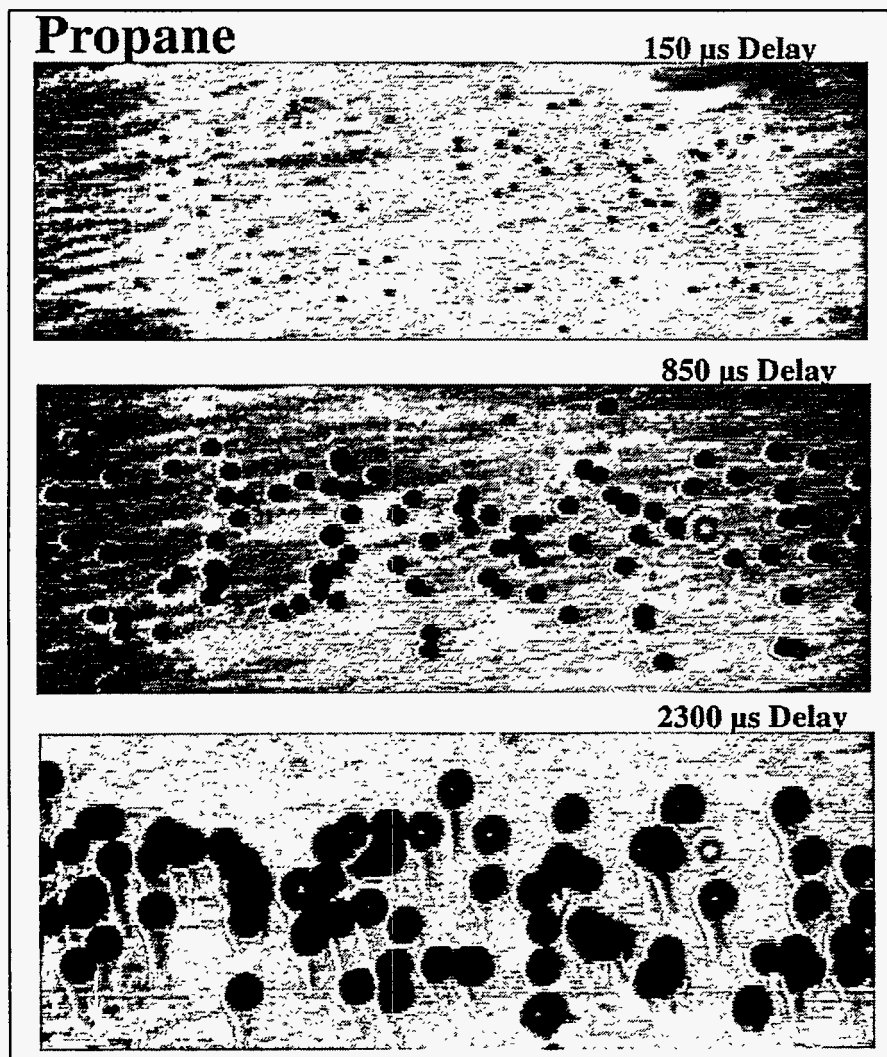


Figure 2. Bubble tracks produced by a beam of frequency doubled Nd-YAG laser in neat propane. Time delays represent the delays between laser pulse and CCD image capture. As the delay increases bubble size increases, at long delays upwards motion can be discerned. The figures have been cropped down from standard video frames to show just the laser track; essentially no bubbles are formed outside the laser path.

Figure 3 displays the number of bubbles produced as a function of laser pulse energy for pure propane, injection of acetone, and CV solutions. This is the bubble chamber spectroscopy equivalent of an absorption versus intensity plot. To validate the use of acetone as a solvent, neat solutions of three grades of acetone were injected to see if they produced bubbles above the neat propane baseline count. Both HPLC and Reagent grades did show a significant increase in the bubble count, but spectroscopic grade acetone was indistinguishable from the neat propane. All dye samples tested used this grade of acetone (Photorex, Baker) as their solvent. It is important to keep the pressure pulse amplitude constant during these measurements because this affects the number of bubbles produced.

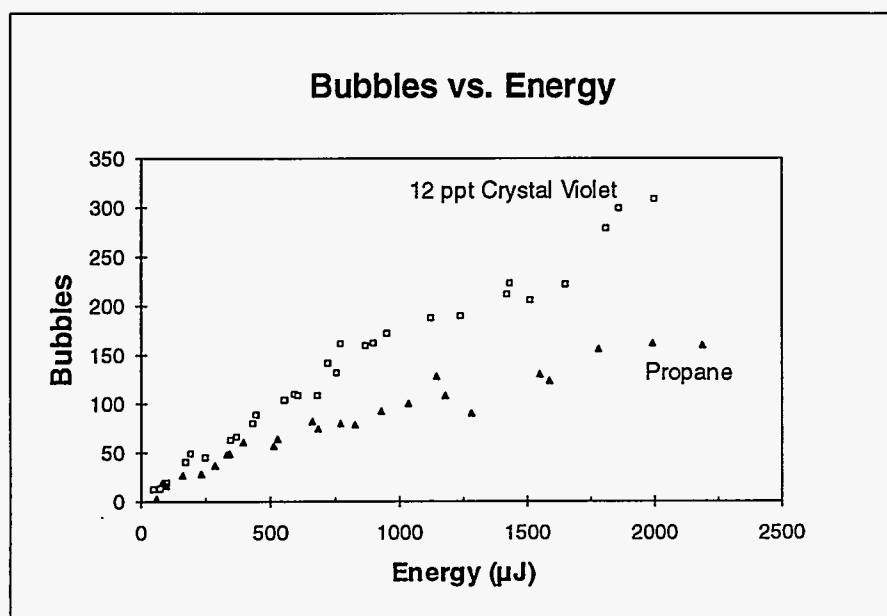


Figure 3. Plot showing near linear relation between number of bubbles formed as a function of excitation energy in neat propane and crystal violet solutions. Figure shows that crystal violet can be detected at the 12 ppt level.

The injection of the test dye (crystal violet in a spectroscopic grade acetone solution) caused a dramatic increase in the bubble count. Even a 12 ppt concentration of dye in the cell was distinguishable from baseline without statistical averaging or multiple laser shots per energy. A 1.2 ppt solution was not distinguishable, indicating the need for reduction of the neat propane baseline. Measurements at higher concentrations show more bubbles per unit of laser energy.

Due to error from bubble overlap (pump laser has a cylindrical cross section in propane) the counts in the high energy regions may be slightly lower than the actual number. A planned upgrade to cylindrical optics will remedy this problem and increase energy sensitivity. Nevertheless the relation between bubble count and energy in both neat propane and crystal violet dye solutions shows a nearly linear relation. All solutions share a common threshold of 40 μJ for bubble formation, but have different slopes for the concentrations of solutes. Although minimal, these preliminary results show quantitatively the sensitivity of the technique. Further experimentation will aid in revealing the quantitative correlation between bubble counts and solute concentration.

4. DISCUSSION

Although the bubble chamber spectroscopy results demonstrate a high sensitivity to absorption and a resulting energy deposition to the medium, we do not yet have a quantitative understanding of the

mechanism. According to classical nucleation theory, under our working conditions of temperature and pressure the minimum energy needed to form a nucleation center would require on the order of a hundred photons.³⁻⁵ Unfortunately, quantitative experimental tests of this theory at the molecular level do not seem to exist. Experimental test measurements of nucleated boiling in homogeneous superheated liquids tend to be fairly insensitive to E_n (the energy of nucleation) because the rate of nucleation changes precipitously at the limiting superheated temperature. Therefore, there is some uncertainty in the actual E_n in our experiments. One possible mechanism is to assume that the observed number of bubbles represents the tail of a Poisson distribution for the absorption of $E_{n/h\nu}$ photons when the average number absorbed is 4 photons per molecule which we calculate from the absorption cross-section. However, this would require closer to 20 photons for E_n and would result in a much steeper curve than that shown in Figure 3. At the current sensitivity we see one bubble for 10^7 absorbing molecules in the laser focal volume. Another proposed mechanism was that the laser beam itself heated the propane slightly, but the calculated temperature increase from absorption in propane is less than 10^{-10} °C. Such a negligible change will not alter the nucleation rate significantly. Although we cannot completely rule out the possibility that the absorbing centers are dye molecule clusters, present in low concentration, which precipitate out when the acetone solution is mixed with the propane; the extremely low concentrations used in the measurements make it unlikely. Tests with less polar dyes, as well as tests at different concentrations of crystal violet should resolve this question. Another possibility is that a dye molecule attaches itself to the small micro particles that may exist in the system and these 'colored' particles form nucleation centers upon absorption of laser light. A system with better filtration is under construction, and experiments with cleaner solvent should clarify this concern.

The linearity of the signal vs. laser energy suggests that the limiting step is a one photon process. This one photon process would generate intermediates which in turn would absorb the multiple photons required for nucleation. There are many possibilities for the character of the intermediate step. It could be a molecular triplet state produced in a small fraction of absorption events;^{10,13} it could be a variety of free radical photo-dissociation products which each absorb more photons;¹⁴ or the intermediate could be a solvated electron produced by multiphoton photoionization that absorbs photons through inverse bremsstrahlung. By examination of several solute types with differing intersystem crossing rates, fragmentation products and ionization potentials it should be possible to sort out the contributions from these different processes.¹⁵ If indeed ionization rather than merely energy deposition is the primary nucleation event, then bubble chamber spectroscopy is more nearly a liquid phase multiphoton ionization detector than a photothermal detector. Regardless of the detailed mechanism, the ability of bubble chamber spectroscopy to observe nucleation from individual molecules provides a uniquely sensitive analytical tool to observe absorption in solution.

5. ACKNOWLEDGEMENTS

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