Measurement of the Bulk Modulus of a Liquid Using a Pump–Probe Laser Technique

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Abstract: We describe an undergraduate laboratory experiment that uses a time-resolved laser technique. Using pump–probe in a novel way, students determined the bulk modulus of a liquid. Employing the fourth harmonic from a pulsed Nd:YAG laser, an elastic wave is generated in an aqueous solution of *N*-acetyltryptophan, and the wave propagation is probed by a He–Ne laser. This experiment serves as a rare example of how a bulk property of a condensed phase can be measured using time-resolved optical measurements having relevance to undergraduate physical chemistry or material science laboratory.

Introduction

Laser-based techniques are ubiquitous in the practice of modern chemistry and are widely used for the study of atomic and molecular structure and chemical reaction dynamics. Recognizing that this trend was not adequately reflected in undergraduate chemistry curricula, chemical educators [1–4] have made concerted efforts over the past decade to design laser-based experiments that are suitable for an undergraduate audience. This is evidenced by recently published experiments in the *Journal of Chemical Education* and in *Developing a Dynamic Curriculum in Physical Chemistry*, edited by Schwenz and Moore [5]. The inclusion of such experiments in undergraduate teaching laboratories has been significantly aided by the availability of inexpensive nitrogen and dye lasers and by generous funding of laser-based projects by the National Science Foundation through *Instrumentation and Laboratory Improvement* (NSF-ILI) grants.

Pump–probe experiments constitute a commonly used technique in laser-based spectroscopy. In a typical experiment, a laser is used to create a species that is subsequently probed with a second laser. This technique is applied to study transient species as well as to follow the progress of bimolecular reactions. In this article we describe a pump–probe experiment with several goals. First, it is a facile introduction to this powerful technique using two commonly used lasers, namely a Nd:YAG laser and a He–Ne laser. Second, it allows the measurement of the bulk modulus of a fluid, an important bulk property, via a novel optical technique. Third, it reinforces the concepts of the measurement of transient phenomena on a submicrosecond time scale using a digital oscilloscope.

Theoretical Background

Determining the bulk modulus of a liquid by applying the fundamental definition, $-V(\partial p/\partial V)_T$, requires enormous pressures to make a reliable measurement. Typical values that have been reported [6] are in the range of 10^4 atm [1]; however, the bulk modulus can be readily determined if the speed of sound in that medium can be measured. In this experiment, absorption of electromagnetic radiation is employed to produce an elastic wave that propagates at the speed of sound. To generate a wave requires a rapid localized perturbation in the equilibrium positions of molecules in a medium. Here, "rapid" means much faster than the motion of the molecules to find a new equilibrium arrangement. In this experiment we will employ a nanosecond pulse from a laser to generate a rapid perturbation.

It is not the pulse that directly generates a perturbation; rather, it is the rapid relaxation of molecules excited by the pulse that creates a thermal shock. Upon absorption of a photon, a molecule is excited into a vibrational level of a higher-energy electronic state as defined by the Franck–Condon principle. This is a process that occurs within a few femtoseconds. Kasha's rule states that an excited-state molecule will rapidly relax ($\sim 10^{-12}$ s) to the ground vibrational level of the first singlet excited state prior to the molecule's relaxation back to the ground electronic state. Return to the ground electronic state can then occur by several parallel mechanisms: emission of a photon (via fluorescence or phosphorescence), internal conversion, and several quenching mechanisms. Within 20 ns following excitation, the molecule will once again find itself in the ground electronic state it originally occupied. If the quantum yield is low in the absence of any significant quenching mechanism, most of the energy gained from absorption of a photon is lost as heat. *It is this rapid release of heat that results in the generation of an elastic wave.*

The optical generation of sound in light-absorbing liquids was first demonstrated over a century ago [7, 8]. With the advent of the Q-switched laser, a detailed analysis of sound excitation with pulsed light was performed [9–11]. As mentioned above, in light absorption a portion of the electromagnetic energy is converted to heat. The thermal expansion that results produces a strain in the medium and a stress wave propagates away from the heated region. For an

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energy input lasting only a few nanoseconds and a media of low thermal conductivity, we assume an adiabatic process. Thus, during propagation of the elastic wave there is negligible heat loss due to thermal conductivity.

A mathematical model developed by Gournay [9] describes the motion of the elastic wave in one dimension for a thermally shocked liquid. Following light absorption, the temperature rise results in a subsequent strain in the medium. An equation of motion derived [9] for an elastic wave generated by the transient heating and subsequent stresses of a liquid is shown below:

$$\frac{\partial^2 u}{\partial x^2} - \frac{\rho}{K}\frac{\partial^2 u}{\partial t^2} = \beta\frac{\partial \theta}{\partial x} \quad (1)$$

where u is the x component of particle displacement, β is the coefficient of linear thermal expansion, $\theta(x,t)$ is the temperature rise due to absorption, ρ is the density of the solution, and K is the bulk modulus. The velocity of the elastic wave, c, is determined from the coefficient of the second term on the left-hand side of eq 1.

$$c = (K/\rho)^{1/2} \quad (2)$$

Thus, by measuring the speed of the elastic wave we can determine the bulk modulus of a medium.

Experimental Section

In this experiment, a solution of *N*-acetyltryptophan (NAT) in a 50 mM sodium phosphate buffer adjusted to pH 7.5 was employed to absorb UV light. For these solution conditions, NAT has a fluorescence quantum yield of 0.14; thus, most of the absorbed light energy degenerates to heat. The NAT concentration was adjusted to provide an absorbance of 1.2 at 266 nm in a cuvette with a 1-cm path length. A 500-μL volume of NAT solution was placed in a 1.00-cm by 1.00-cm by 4.00-cm quartz cuvette with four polished sides.

The output from a Q-switched neodymium–yttrium–aluminum–garnet (Nd:YAG) laser was used as a pulsed light source (see Figure 1). The fourth harmonic (266-nm light) of the fundamental frequency was generated using two nonlinear crystals housed within the laser. The fourth harmonic was separated from the fundamental and the second harmonic using an optical assembly provided with the laser system. The temporal profile of the pulse had a full width at half the maximum intensity of 6 ns. The average power was 10–20 mJ/pulse.

The incident laser beam is positioned normal to the face of the cuvette (see Figure 1). Whereas a collimated beam is rapidly attenuated by passage through a strongly absorbing medium, the incident beam is focused 1.0 cm in front of the face of the cuvette so the beam intensity decreases sharply from its initial entry into solution. Thus, the greatest density of molecules in the excited state will occur at the entry point of the incident beam. Excited-state molecules relax back to the ground state by nonradiative processes that occur at a much faster rate than dissipation of the resulting heat, and an elastic wave arises from the thermally shocked liquid.

The wave velocity was measured by the pump–probe setup shown in Figure 1. The excitation pulses are split into two beams using a beam splitter. The less intense beam falls on the fast photodiode, PD1, whose output signal triggers the input on the oscilliscope. The remaining light excites the sample. A helium–neon laser provides a continuous source of 633-nm light that is used as the probe beam. The probe and excitation beams intersect at 90° within the cuvette. The probe beam that exits the cuvette is aligned through a narrow opening of an iris into a second fast photodiode, PD2.

The signal from PD1 triggers a 400-MHz digital oscilloscope to begin recording the signal intensity from PD2 over time. Signal-to-noise was improved by summing 50 scans. Please see the supporting material for a brief handout given to the students when we implement this experiment in our undergraduate laboratory course.

Results, Data Analysis and Discussion

The elastic wave generated by the excitation pulse travels orthogonally past the probe beam as it reflects back and forth in the cuvette. Each time the wave passes through the beam, the accompanying change in the refractive index of the medium changes the beam's trajectory. Consequently, the beam is periodically not aligned to pass through the iris aperture and a periodic dip in the signal intensity of PD2 results in a series of peaks with negative amplitude (see Figure 2). Intensity of these peaks decreases with every passage past the probe beam, which reveals the rate of energy loss from the elastic wave to the solution as heat.

The round-trip time can be determined by measuring the delay between peaks 1 and 3 or 2 and 4. Measuring delays between consecutive peaks is misleading, because they will vary with the position of the probe beam. If the probe beam is not positioned to go through the exact center of the cuvette, the time between the first and second peaks will differ from the time between the second and third peaks; however, we found that the time between the first and third peaks will always be the same as the time between the second and fourth peaks. Knowing that the round trip distance is 2.00 ± 0.02 cm, we can determine the speed of the wave in the medium.

We measured the speed in water and in two aqueous solutions of salt water of different concentrations (listed in Table 1). Each value was within 1% of the reported [12] speed for sound in the respective solution. Determination of the bulk modulus also requires an accurate value for the density of the medium, which is a function of temperature. A thermocouple was placed in direct contact with the medium to measure the temperature. The repetition rate of the YAG laser was set at 0.1 Hz to provide plenty of time for heat to dissipate between pulses. Prior to collecting and adding together time scans, the sample was pulsed for two minutes, allowing the medium to arrive at a steady-state temperature. A temperature of 29 ± 0.5 °C was maintained during the pump–probe measurements. Values for the densities of the solutions at the temperature used in these experiments are readily available [12].

Using Equation 2, we are able to determine the bulk modulus of the several solutions (see Table 1). We observed that as the NaCl concentration increases the speed of sound increases, as does the bulk modulus. Thus, we present here a reliable way for making an otherwise difficult measurement in an undergraduate laboratory setting.

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Table 1. Bulk Properties Determined for Aqueous Solutions

Aqueous solution	Density g mL^{-1}	Measured speed of wave $\pm 2 \times 10$ m s^{-1}	Speed of sound[a] m s^{-1}	Bulk modulus $\pm 4 \times 10^4$ Pa
water	0.996	1480	1486	2.18×10^6
3.5 wt % NaCl	1.023	1530	1521	2.39×10^6
6.0 wt % NaCl	1.041	1555		2.52×10^6

[a]Speed of sound reported [12] for aqueous solutions at 29 °C.

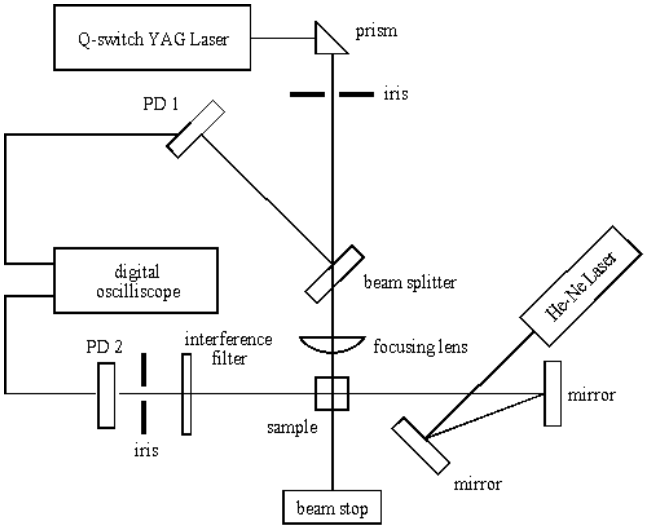

Figure 1. Schematic of the laser system. PD1 and PD2 indicate the positions of photodiode 1 (generates the trigger signal for the oscilloscope) and photodiode 2 (measures the intensity of the transmitted He–Ne beam).

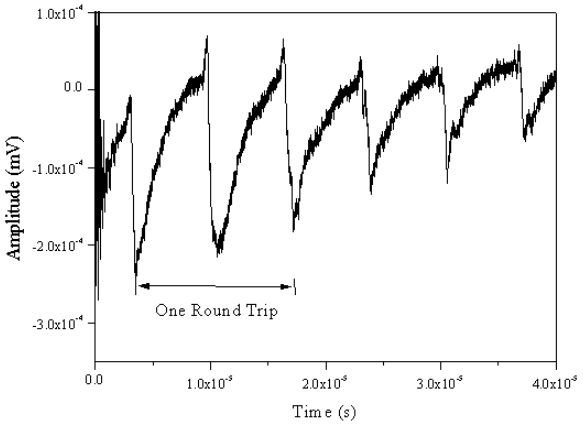

Figure 2. Variation in the intensity of the transmitted He–Ne beam reaching the photodiode (PD2) following pulsed excitation of the sample with 266-nm light. Negative peaks represent a periodic decrease in intensity resulting from the deflection of the He–Ne beam as the acoustic wave propagates past the beam. The arrow displayed in the figure indicates the round-trip time for the acoustic wave.

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Supporting Material. The student instructions for carrying out this experiment in the laser laboratory is available as an Adobe Acrobat PDF file (http://dx.doi.org/10.1007/s00897010489b).

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