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QUANTITATIVE SPECTROSCOPY OF WEAKLY ABSORBING CONDENSED MEDIA

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1. INTRODUCTION

Weakly absorbing features of condensed media often contain significant information important in the structure of materials as well as in the application of the materials to technology. In the last ten years revival of an old technique[1] has led to major advances in our ability to quantitatively measure spectroscopic features of weakly absorbing gases,[2] liquids[3] and solids.[3,4] This technique, called opto-acoustic spectroscopy by the scientists responsible for its early development and demonstration of its capabilities, relies upon nonradiative decay of the absorbed energy to heat the illuminated volume and the subsequent detection of heat as an acoustic signal. The opto-acoustic technique when applied to gaseous media was shown[5] to be capable of measuring absorption coefficients as small as $\sim 10^{-10}$ cm^{-1}. But similar ability to measure small absorptions in condensed media was not shown until 1978 in spite of a straightforward extension of the early gas phase studies to liquids and solids[6] in 1973. Recently, a consideration of acoustic impedance mismatch between the medium in which the acoustic signal is generated and the transducer that detects the pressure signal has led to the development of pulsed laser immersed (for liquids) or attached (for solids, powders and thin films) piezoelectric transducer opto-acoustic scheme which has been shown to be capable of measuring absorption coefficients as small as $\sim 10^{-7}$ cm^{-1} in condensed media. In this paper I will review the technique and describe its applications to measurement of weak absorption spectra in the visible and infrared region arising from linear as well as nonlinear interaction of radiation with materials. The linear studies include spectroscopic studies of organic and inorganic liquids, thin films, powders and solids. The nonlinear processes so far studied include two photon absorption and stimulated Raman scattering. Further, I will describe the opto-acoustic spectroscopy of solids and cryogenic liquids at temperatures as low as $\sim$1.2K. Finally, I will mention the extensions of these opto-acoustic studies to other areas including the initial excitation provided by sources other than optical ones, e.q., X-ray and electron beams.

2. SIGNAL GENERATION

When a liquid or solid is illuminated by a pulsed optical radiation at a frequency ν, the absorbed energy, $E_{abs} \simeq E_o \alpha \ell$ for $\alpha\ell \ll 1$, where E_o is the incident pulse energy, α is the optical absorption coefficient, and ℓ is the sample length, is lost by either radiative or nonradiative means. In case of primarily nonradiative relaxation, the illuminated cylindrical volume (see Fig. 1) undergoes a transient expansion (or contraction, depending upon the size of the thermal expansion coefficient) which launches in the medium an acoustic pulse consisting of a compression followed by a rarefaction pulse. The duration of the acoustic pulse (defined as the time separation between the compression and rarefaction waves) is approximately given by the shorter of the two times - the optical pulse with τ_p, and the acoustic transit time τ_a across the illuminated

cylindrical volume given by $\tau_a = R/v_a$ where 2R is the diameter of the optical beam and v_a is the acoustic velocity. This acoustic pulse, as has been shown,[3] can be detected very efficiently by a piezo-electric transducer because of the good acoustic impedance match between the liquids and solids and the transducer. The opto-acoustic voltage V_{oa} generated is given by

a) For $\tau_p >> \tau_a, \tau_r$

$$\frac{V_{oa}(\nu)}{E_o(\nu)} = K_p \frac{\beta v_a}{C_p} \alpha(\nu) \qquad (1)$$

b) For $\tau_r > \tau_a$, and $\tau_a > \tau_p$

$$\frac{V_{oa}(\nu)}{E_o(\nu)} = K_a \frac{\beta v_a^2}{C_p} \left(\frac{Z_{abs}}{Z_{abs}+Z_{pzt}} \right) \alpha(\nu) \qquad (2)$$

c) For $\tau_a > \tau_p, \tau_r$,

$$\frac{V_{oa}(\nu)}{E_o(\nu)} = K_r \frac{\beta v_a^2}{C_p} \alpha(\nu) \qquad (3)$$

where β, and C_p, are the volumetric thermal expansion coefficient, and the specific heat at constant pressure of the medium, K_a, K_p, and K_r are constants which are determined by specific geometry, transducer responsitivity, etc., and Z_{abs} and Z_{pzt} are the acoustic impedances of the absorber and the piezo-electric transducer, respectively. References 3, 7 and 8 should be consulted for details.

A crucial requirement of any spectroscopic technique is its ability to yield quantitative absorption data. The β, v_a, and C_p as well as Z_{abs} and Z_{pzt} are known for most materials. The K's can be evaluated from first principles thus allowing us to obtain $\alpha(\nu)$ from measured $V_{oa}(\nu)/E_o(\nu)$ in Eqs. (1)-(3). In practice, it is more convenient to use a "doped" sample technique for evaluating K's and then transferring the calibration to different materials through sealing using known β, v_a, C_p, Z_{abs} and Z_{pzt}. This technique described in detail in Ref. 3 has turned out to be very successful and is commonly used.

3. EXPERIMENTAL TECHNIQUES

Typically, the optical rediation is provided by a pulsed laser. We have used either a flash lamp pumped dye laser or a doubled Nd:YAG laser pumped laser as the sources. These provide $\gtrsim$ 1 mJ of laser energy in $\sim$1-2 μsec or $\sim$7-10 nsec duration pulses, respectively. The piezo-electric transducer (lead zirconate-titanate piezo-electric ceramic) is enclosed in a stainless steel enclosure as in Fig. 2 to minimize the problems[9] arising from scattered light hitting the

bare transducer and from RfI pickup in the presence of pulsed lasers. Typical experimental opto-acoustic cells for liquids, powders (or thin films) and solids are shown in Figs. 3 and 4. The entire experimental setup is shown in Fig. 5. A convenient acronym for the PUlsed Laser PIezo-electric Transducer detection method is PULPIT opto-acoustic spectroscopy.

While pulsed dye lasers are tunable only over the visible region, long wavelength PULPIT opto-acoustic spectroscopy has been demonstrated recently[10] up to a wavelength of ∿1.6 μm by using a high pressure hydrogen cell for down shifting the dye laser frequency by I and II Stokes stimulated Raman scattering.

4. SENSITIVITY

By carefully studying the PULPIT opto-acoustic spectra arising from 6^{th}, 7^{th} and 8^{th} harmonics of C-H vibration of benzene[3] (see Section 5, also), we have ascertained that using a laser pulse energy of ∿1 mJ and pulse repetition rate of 10 Hz, we can measure absorption coefficients as small as $\sim 10^{-7}$ cm^{-1}.

This limit at present appears to be set by preamplifier noise rather than extraneous signals arising from window absorptions (in the case of liquids), substrate or surface absorption in the case of powder (thin films) and solids or electrostriction. These points are discussed in detail in Refs. 3 and 11. I would like to make one point, however. There has been considerable confusion recently, primarily caused by results of Brueck, et al.[12] regarding the importance of limitation arising from electrostriction. We have shown[3,11] that electrostriction is not a limiting consideration at levels of $\alpha_{min} \gtrsim 10^{-7}$ cm^{-1} and further improvements should be possible to reduce α_{min} below the 10^{-7} cm^{-1} level by improved transducers, preamplifiers and increased pulse energies.

5. APPLICATIONS OF PULPIT OPTO-ACOUSTIC SPECTROSCOPY

The demonstrated ability to measure optical absorption coefficients as small as 10^{-7} cm^{-1} in bulk condensed media, and ability to measure $\alpha\ell$ as small as $\sim 10^{-7}$-10^{-6} in the case of thin films and powders has made the PULPIT opto-acoustic spectroscopy a powerful tool for the quantitative study of absorption spectra of weakly absorbing media. In the following I list some of these and make comments on recent studies.

a. Linear Spectroscopy at Ambient Temperatures

Aromatic Hydrocarbons: Absorption data on 6^{th}, 7^{th} and 8^{th} harmonics of benzene[3] and on 6^{th} harmonic of substituted benzenes[13] such as chlorobenzene, bromobenzene, etc., have been obtained. Peak absorption coefficients range from $\sim 10^{-3}$ to 10^{-5} cm^{-1}. These data together with similar gas phase data promise to allow a proper theoretical treatment of local environment effect on overtone spectra in liquids.

H_2O and D_2O: Accurate absorption spectra of H_2O and D_2O have been obtained in the visible region.[3]

Thin Liquid Films:[3] Thin liquid films of $NdCl_3$, $PrCl_3$, and $HoCl_3$ (1-5 μm thick) have been measured and show that the technique is capable of measurements of monolayer thick films.

Powders: High resolution spectra of Dy_2O_3, Er_2O_3 and Ho_2O_3 have been obtained.[3] These studies show that PULPIT opto-acoustic spectroscopy is ideally suited for measuring weak absorption spectra highly scattering compounds. This ability may

turn out to be important in exploratory studies of low loss materials for long wavelength optical fibers,[14] and for the study of biological suspensions.

b. Nonlinear Spectroscopy:

At high intensities available with pulsed lasers, nonlinear absorption processes are known to be important. These nonlinear absorptions, however, are small and thus PULPIT opto-acoustic absorption spectroscopy is ideally suited for such studies.

Two Photon Absorption Spectroscopy: Focused laser radiation has been used to carry out PULPIT two photon absorption spectroscopy of benzene$_3$(A_{1g}-$^1B_{2u}$ band). First two photon absorption cross-sections have been obtained.

Raman Gain Spectroscopy: By having two pulsed laser radiations at frequencies separated by a Raman allowed transition frequency of the medium, Raman gain PULPIT opto-acoustic spectroscopy of a variety of liquids such as benzene has been demonstrated.[3] Ability to measure Raman gains as small as $\sim 10^{-5}$ cm^{-1} is demonstrated.

c. Low Temperature Spectroscopy

As long as the temperature is below the Curie temperature of the piezo-electric transducer, PULPIT opto-acoustic spectroscopy has no lower temperature limit. Thus by appropriate reconfiguration of the opto-acoustic cells low temperature liquids and gases can be studied.

Liquids: High quality absorption data of liquid methane[15] and ethylene[10,16] with the latter extended to long wavelengths have been obtained at temperatures as low as 90 K.

Solids: Recently we have obtained[17] overtone vibrational spectra of solid hydrogen (see Figs. 6 and 7). The second and third harmonic spectra of solid hydrogen show many differences compared to similar data for collision induced spectra in high pressure hydrogen. The data on hydrogen should be crucial in obtaining deeper understanding of the simplest molecular solid - hydrogen.

Solids of Technological Interest: To obtain absorption spectra of solids of practical importance, such as materials for low loss optical fiber, it is seen that room temperature is not the ideal place to work. It is seen that the sensitivity of PULPIT opto-acoustic spectroscopy can be considerably enhanced by carrying out the measurements at low temperatures as seen in Fig. 8 for SiO_2. Notice that the low loss measurement capability of $\sim 10^{-7}$ cm^{-1} corresponds to $\sim$0.2 dB/kM. Similar temperature dependence is seen from other materials - e.g. semiconductors. We are, at present, pursuing some of these studies.

6. CONCLUSION

PULPIT opto-acoustic spectroscopy is clearly making major impact in the quantitative study of weak absorption spectra of liquids, thin films, powders, and solids at temperatures as low as 1.2 k. While I have only briefly touched on some of the studies already carried out, the future is equally promising. These future directions include 1) higher order Raman process studies, 2) materials testing, 3) trace and impurity detection including biological systems, 4) forbidden transitions and effect of electric, magnetic fields, etc., 5) excited

state studies, 6) monolayer absorption spectroscopy, 7) opto-acoustic microscopy, and 8) electron beam and X-ray excitation acoustic detection.

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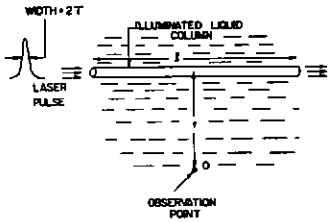

Fig. 1. Schematic of pulsed opto-acoustic detection.

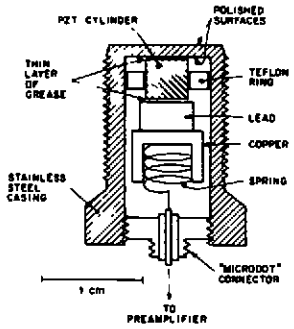

Fig. 2. Details of piezo-electric transducer assembly.

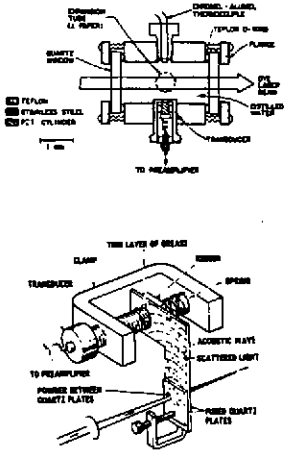

Fig. 3. Experimental geometries for liquids and thin films.

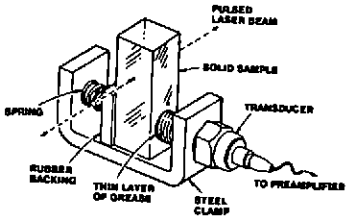

Fig. 4. Experimental geometries for solids.

QUANTITATIVE SPECTROSCOPY OF WEAKLY ABSORBING CONDENSED MEDIA

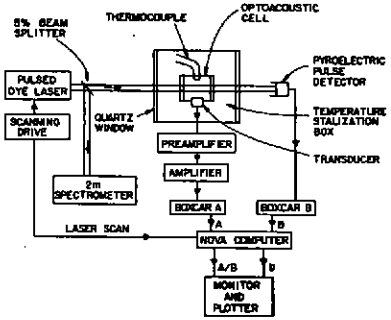

Fig. 5. Experimental setup

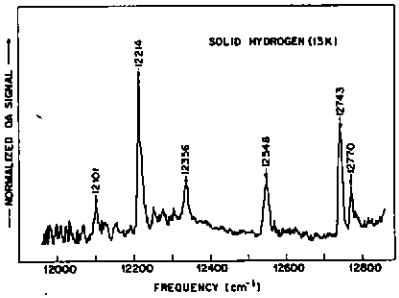

Fig. 6. PULPIT opto-acoustic absorption spectra of solid hydrogen (0-3 band).

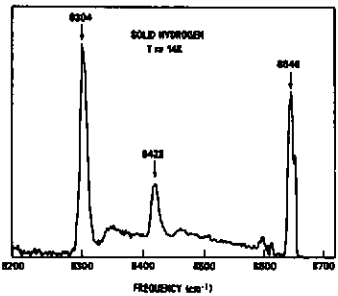

Fig. 7. PULPIT opto-acoustic absorption spectra of solid hydrogen (0-2 band).

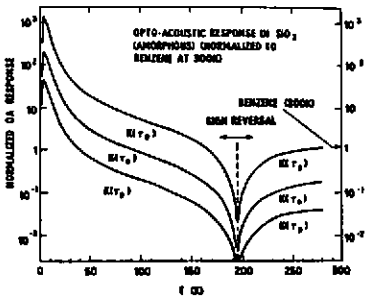

Fig. 8. PULPIT opto-acoustic detection sensitivity for SiO_2 as a function of temperature.