Photothermal Deflection in a Supercritical Fluid

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Photothermal deflection is among the most sensitive techniques available for the measurement of small, localized heating, such as that from the absorption of a focused laser beam in the bulk or surface of a material. A thin optical probe beam is deflected by the refractive-index gradients arising from the heating, and the size of the deflection provides the measure of the heating. We describe the use of a critical fluid to enhance the sensitivity of the technique by at least 10³. The diverging coefficient of thermal expansion of a pure fluid near the gas-liquid critical point gives this dramatic enhancement when used as a sensing fluid. With sensitivity calculations and measurements in supercritical xenon, Tc ≈ 16.7°C, we show that the noise floor of our apparatus when used for surface absorption measurements corresponds to a fractional power absorbed of \( P_{\text{absorbed}} / P_{\text{incident}} = 10^{-10} \), while the noise floor for bulk measurements corresponds to an absorption coefficient \( \alpha = 10^{-13} \text{ cm}^{-1} \). We report the first measurements of the surface absorption of superpolished surfaces of sapphire and fused quartz, \( P_s / P_i = 2 \times 10^{-7} \), and the first measurements of the bulk absorption in xenon, \( \alpha \approx 2 \times 10^{-6} \text{ cm}^{-1} \). We also show how the present work fits into the current status of absorption measurement techniques and describe the effects of the peculiar properties of critical fluids on the execution of photothermal deflection measurements.

KEY WORDS: absorption; critical; photothermal deflection; photothermal method; spectroscopy; supercritical; surface.

1. INTRODUCTION

The most sensitive techniques available for the detection of very small temperature gradients in transparent materials are optical techniques. A probe beam passing through a heated region is deflected and suffers a phase shift from the refractive-index gradients that arise from thermal expansion.

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These effects can be used in experiments on both bulk materials and surfaces, as depicted in Fig. 1. There are many photothermal spectroscopies, where an excitation is created by the absorption of radiation and decays mainly by thermal diffusion. The strength and dynamics of the signal in these techniques provide information about the processes governing the heating—for example, the relaxation of electrons and heat excited in a semiconductor surface by a pulsed pump laser can be monitored from the resulting heat in a fluid above the surface [1], and the presence and concentration of impurities in transparent samples can be deduced from the heat generated by the absorption of a laser beam in the bulk of the sample. The number of applications has grown with the widespread availability of powerful lasers and high-resolution position sensors for optical beams.

This paper describes the enhancement to these techniques through the use of a supercritical fluid as the sensing fluid. The enhancement arises because the signal is created from the thermal expansion of the sensing fluid and the thermal-expansion coefficient of a pure fluid diverges as the state of the fluid approaches the liquid–vapor critical point. At the critical density $\rho_c$ and at a temperature $10\,\text{K}$ above the critical point of xenon, $T_c = 16.7\,\text{K}$, the isobaric thermal-expansion coefficient $\beta_p = (1/\rho) \partial \rho/\partial T = 9 \times 10^{-2}\,\text{K}^{-1}$, about $100\times$ larger than noncritical fluids. By $T - T_c = 1\,\text{mK}$, $\beta_p$ has further increased by 4 decades. By using a sample of supercritical xenon in a photothermal-deflection apparatus, we measure three decades enhancement over the sensitivity reported by other workers with noncritical fluids, making the supercritical method far more sensitive than any other available.

We do not discuss the details of either the calculations of the apparatus here; these are sufficiently important and lengthy to reserve for