

Design and Construction of a compact monoblock for gas phase mirage effect spectroscopy

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We have developed a monoblock cell based on mirage effect (Photothermal beam Deflection, PTD) spectroscopy for trace gas detection in a variety of practical applications capable of real time measurements at the part per billion (ppb; $1:10^9$) an sub-ppb level in controlled environments or in open air. Our principal objective of this design has been in improve the sensitivity and flexibility of operation, developing a new alternative for a gas detection systems. We discuss the implication of our design and construction choices and also mention many practical applications of this instrument.

Keywords: Mirage effect spectroscopy; Photothermal deflection; Environmental monitoring

1. Introduction

Photothermal beam deflection, or mirage effect spectroscopy, is a photothermal technique similar to Photoacoustic spectroscopy (PA), with sensitivity roughly on the same order of magnitude. The PA spectroscopy commonly restricts its operation to a closed cell, which may be made quite small [1], but requires a gas delivery and sampling system, precluding open air measurements. If an open cell is used, a buffer volume must be incorporated which leads to larger working volumes. Since PA spectroscopy measures pressure waves, temperature and vibration stability may also be critical to assuring the quality factor of the resonant cell, and in no case may local probing of a sample be performed. The mirage effect is a technique that may be applied in an initial trace gas monitoring study [2], upon which we base our current work. The setup is shown schematically in Fig. 1. Gas phase mirage effect detection also relies on the resonant absorption of a modulated (pump) laser source within the volume to be analyzed. The hereby created periodic temperature rise is probed by a second laser beam which is deflected by the local refractive index gradient induced by the thermal gradient in the heated region. The deflection angle (ϕ) is a measure for the concentration of absorbing molecules, the expression for the deflection beam in parallel PDT has been developed as [3-4]:

$$f = -2 \left(\frac{x_0}{a_p^2} \right) \frac{1}{n} \left(\frac{dn}{dT} \right) \frac{P}{w r p^2 a_p^2} [1 - \exp(-\alpha l)] \exp\left(\frac{x_0^2}{a_p^2}\right) \quad (1)$$

Here, the parameters, grouped by class are n , $\frac{dn}{dT}$, r , and c : gas (mixture) index of refraction, variation of index with respect to temperature, density, and specific heat, respectively, α : gas (absorbing species) absorption coefficient; x_0 and l : separation distance between the axis of the two beams and interaction length, respectively; and P , w and a_p : pump laser power, modulation frequency, and

pump beam's waist at $1/e$ intensity, respectively. This expression holds for modulation frequencies for which the thermal diffusion length (a_s) is smaller than the pump beam waist (a_p), for pump beam waist $a_p > a_s$ (probe beam waist, and interaction length (l) shorter than the Raleigh length (z_0)). For weak absorption, the parallel distance can be maximized, and the equation (1) takes the form:

$$f = C_g \alpha \frac{P}{w a_p^3} \quad (2)$$

Here C_g depends on physical parameters of the entire gas mixture, while α is the concentration adjusted absorption coefficient of the absorbing species in the mixture. The parameters P , and w depend on the laser operation, while l and a_p depend on (fixed) optical parameters of the setup [5].

On the other hand the advantages of our technique with respect to PA spectroscopy include the possibility to perform local detection, and reduced restrictions on detection cell geometry, which permit open air detection with more flexibility in practice. The geometry of the current design is quite compact (34 cm), and incorporates a well defined, truly parallel interaction region between the pump and probe beams. Our proposed design results in mirage block with more compact size, more flexibility, and resistance to atmospheric turbulence, while retaining the capability to perform measurements on a local scale, we believe this design to be an intermediate step between laboratory setup and industrial application which could be transported with minimal modification, at the cost of reduced absolute sensitivity and control.

2. Description of the monoblock design and construction

Photography of the new block is shown in Fig. 2. The most novel geometric characteristic of the new cell is the use of two-germanium (Ge) disks, which confine the

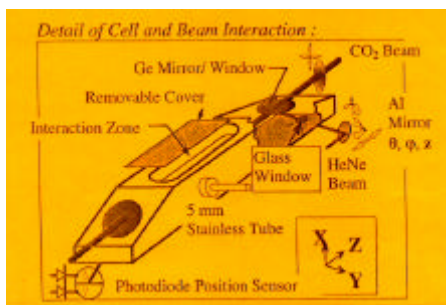


Figure 1 Detail of Cell and Beam Interaction



Figure 2 Cell photography

interaction region of the detection cell. Improvements in the purity of this material make possible optical components with very little residue. As this material is transparent in the IR range and reflective in the visible, the disks act as mirrors for the HeNe probes beam, and act as windows for the CO₂ pump beam (see reference [6]). To minimize transmission losses, the disks are set at the Brewster angle (76°) at $10.6 \mu\text{m}$, the nominal-working wavelength. This detection cell forms the principal component of the setup; other components include the pump laser and associated ZnSe lens, probe laser, focusing mirror and the photodiode detection assembly (it is not shown here). The trapezoidal detection cell body, shown in Fig. 2, is machined from a single aluminum block to assure vacuum integrity. The inclined ends of the cell are closed by the two Ge disks, each fixed in place by removable holders. The holders incorporate O-ring seals and are fashioned in stainless steel to reduce stress on the brittle Ge disks during assembly. The linear interaction length between the two disks is 20 cm.

The laser paths are formed by simple holes drilled through the block, with a larger, rectangular central space. This space is large enough to permit the placement of solid samples for gas emission studies; the entire interior volume is 25 ml, from this volume, the interaction volume is estimated to be 0.0125 ml. The top of the cell may be closed by a cover and a flat rubber seal. Glass windows seal the entry holes for the probe beam. Two manifold mounted 5 mm tube Hoke terminator connect a pressure tap and gas handling system to the detection cell. The gas handling system is used to introduce calibrated mixtures to the closed cell. For *in situ* atmospheric measurements, the top of the cell is simply removed. We characterize the optical alignment through the cell cavity obtaining optimal results, also a good optical and mechanical stability was observed which show the robust and compact design at minimum cost.

3. Objectives in our future investigations

Our objectives for the future work are: demonstration of an instrument for trace gas detection capable to measure:

- Important pollutant species; Ozone, and NH₃, single or in a mixture

- *In situ*; on site and in open air
- In real time

Our objectives for the technical characteristics are:

- Sensitivity better than 1ppb ($<10^{-9}$)
- Selectivity of multiple species in a mixture (or air)
- Response on the time scale of seconds, stable for hours

Applications to be investigate:

- In vivo study
- Study communication within the plant itself
- Use of plants as biomonitor of toxines
- Study of plants with biomaterial
- In vivo study of microbacterias

4. Conclusions

We present a compact and rugged mirage block developed here for real time *in situ trace* gas detection based on photothermal beam deflection spectroscopy. The use of high quality Ge windows permits a true parallel geometry, resulting in a resistant design to ambient air motion while preserving the advantages of the technique such as good sensitivity to local probing, and open-air measurement capability. Our objectives in the future are the measurement of absorption spectra in open cell air and ethylene exhaust at real time from biological samples to investigate industrials, agricultural, and environmental applications.

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