

Improved Spectrometer for Long Path Length Absorbance

(Variable Pathlength Cavity Spectroscopy)

(OTT 1207)

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Ultra-Trace Analysis by Molecular Absorption Spectroscopy

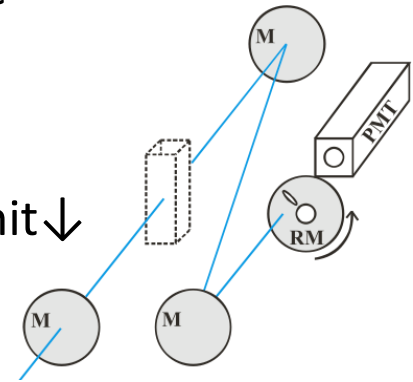
- ❑ Ultra low level concentration measurements require highly sensitive detectors and/or a long pathlength in order to yield useful data
- ❑ This adds to cost and the footprint of the spectrometer
- ❑ Spectroscopy systems are limited in the measurable concentration range by the optical path configuration

Variable Pathlength Cavity Spectroscopy (VPCS)

- ❑ The ability to increase the effective pathlength and send all available light to the detector allows for measurement of extremely dilute samples
- ❑ VPCS allows precise control of the intra-cavity resonance times and the consequent ability to tune the pathlength amplification for a given sample over several orders of magnitude
- ❑ The system is versatile; liquid flow-through spectroscopy and evanescent wave measurements of condensed phase samples are possible with the addition of the dove prism configuration
- ❑ This technology may also be applied to flow injection, gas chromatography, liquid chromatography, and capillary electrophoresis

- We are developing a novel approach to ultra-trace analysis by molecular absorption spectroscopy. In VPCS, the absorbance enhancement is determined by the amount of time that the light can stay inside the cavity, and thus the number of times that the light can pass through the sample

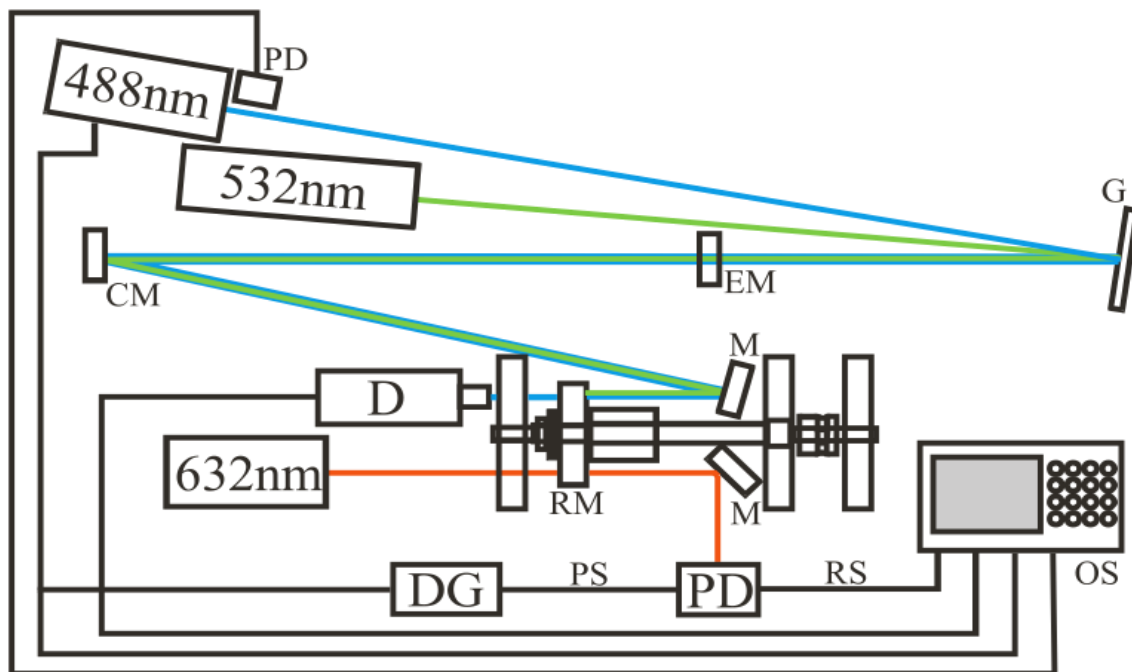
- Time Within Cavity \uparrow = Distance Traveled \uparrow = Detection Limit \downarrow



- VPCS allows for the manipulation of the time that the light spends within the cavity, thereby increasing the dynamic range of the measurable absorbance
- This slide deck will describe the design of the spectrometer for one of the four prototypes constructed, summarize the results of optimization studies, and present performance data for the monitoring of trace levels of nitrogen dioxide in ambient air

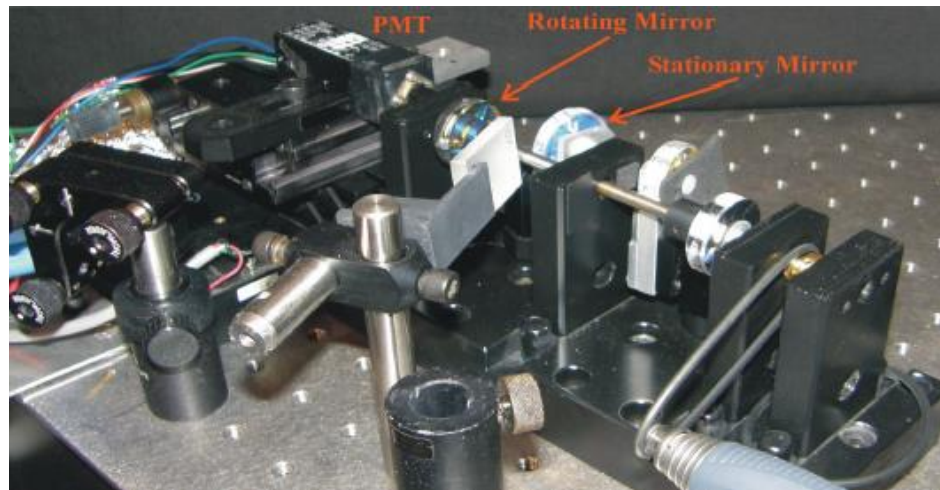
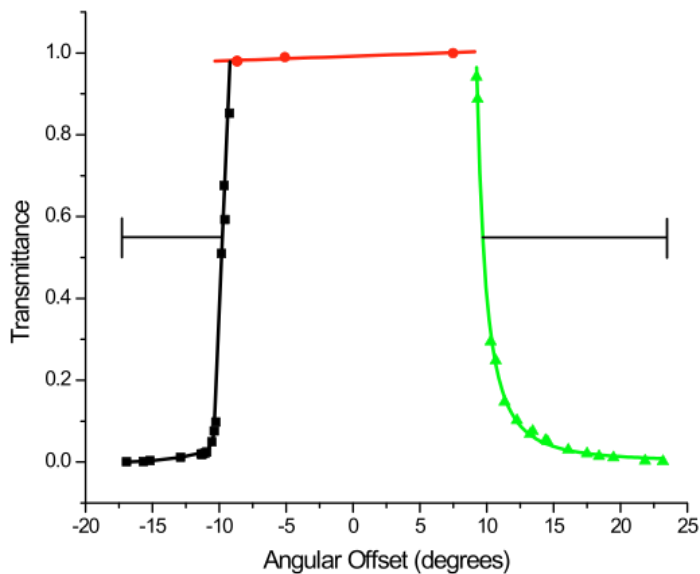
Variable Path Length Cavity Spectroscopy

- ❑ A high-finesse optical cavity is created by use of a flat, rotating mirror of high reflectivity. Light from a dye laser (488 nm) enters the cavity by transmission through a highly-reflective dielectric mirror, in the same way as in Cavity Ring-Down Spectroscopy (CRDS)
- ❑ Unlike CRDS, the optical configuration allows for the absorbance data to be recorded directly



PD (photo diode), G (diffraction grating), EM (entrance mirror), CM (concave mirror), M (mirror), D (detector), RM (rotating mirror), DG (delay generator), PS (processed signal), RS (raw signal), OS (oscilloscope)

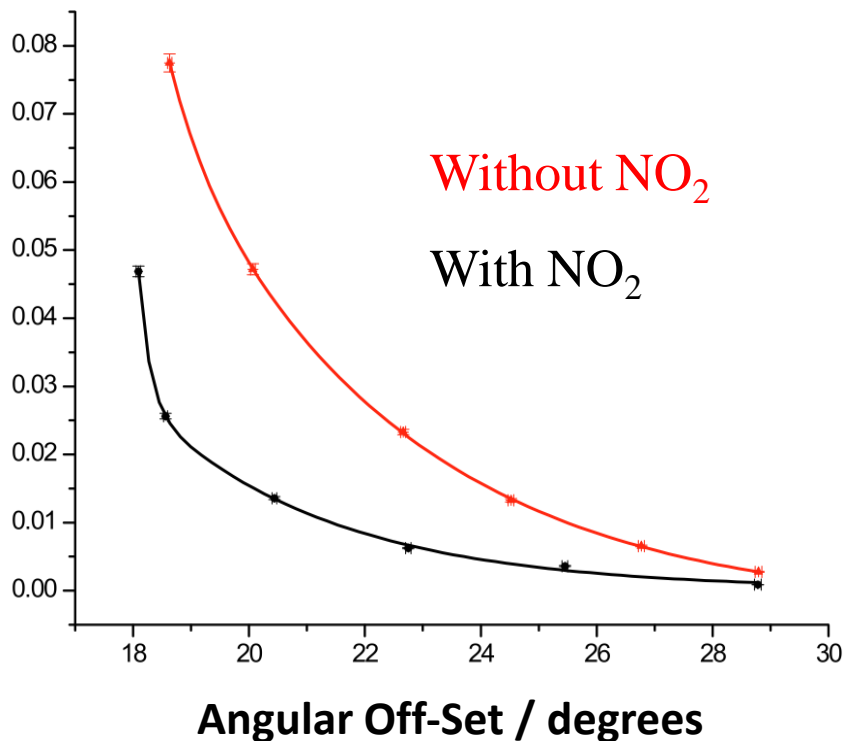
The Effect of Angular Offset on Transmittance



A VPCS Prototype

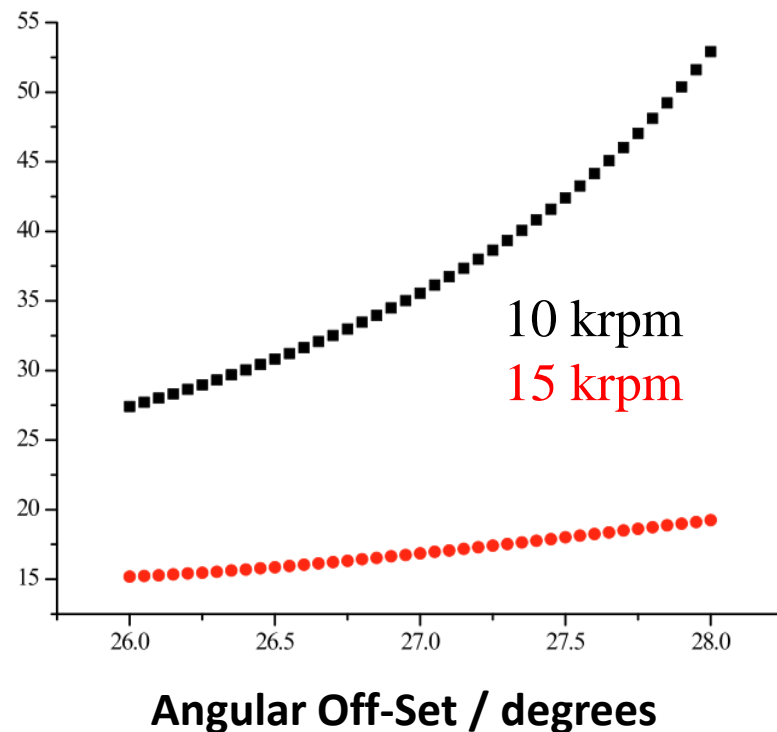
The decay observed at the trailing edge of the slit (negative values) shows the interaction of the beam with the edge of the slit. This “edge effect” is convoluted into the results observed on the leading edge of the slit (positive values). Evidence that trapping is taking place is shown by observing the maximum angular offset in each direction. Note that $+\theta_{\max}$ is almost double $-\theta_{\max}$.

NO₂ Measurement



A decrease in the transmittance was observed when the angular off-set was increased, demonstrating in principle that light was effectively trapped in the cavity.

Measured Enhancement



Variation of the frequency of mirror rotation resulted in changes in transmittance that agreed with theoretical predictions. The enhancement factor is the ratio of the pathlength increase (b*) to the conventional cell (single-pass) pathlength (b).

U.S. Utility Patent US 9,013,700

Variable path length photon trapping spectrometer

Current Status

- Seeking development partners for testing to aid in final product
- Technology is available for licensing under exclusive or non-exclusive terms

- ❑ Variable Pathlength Cavity Spectroscopy has been performance tested using nitrogen dioxide (1.28mM), showing a calculated 50 fold pathlength enhancement
- ❑ Initial testing on the transmittance with variation in the frequency of the mirror agreed with theoretical predictions
- ❑ The system is compact and has demonstrated the ability to accurately vary pathlength

- Automating the instrument control and data acquisition & processing functions
- Improving vibration damping to stabilize the beam alignment
- Examining ways to more precisely fabricate the mirror slit
- Expanding the application of the technique to condensed phase samples using a Dove prism flow cell

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