

# New Laser Techniques for Detection of Radicals, Isotopes, and Reactive Intermediates from Robotic Aircraft and Conventional Aircraft for the Aura Satellite Collaborative Science Effort

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**Abstract**-Economic development, the protection of life and property, and stewardship of the planet for this and future generations are increasingly dependent upon decision structures based upon innovation and discovery in the Earth Sciences. We report here on selected developments in laser technology applied to *in situ* detection of trace concentrations of free radicals, isotopes, reactive intermediates and tracers of atmospheric motion. Focus of the presentation will be on the coupling of QCL, DFG, and fiber lasers to high-finesse cavities using Cavity Ringdown Spectroscopy and Integrated Cavity Output Spectroscopy deployed from the NASA WB-57 high altitude aircraft as a preamble for deployment on UAVs. The research support from this NASA IIP project addresses the development of robust, miniaturized laser systems to attack problems in tropospheric and stratospheric chemistry, dynamics and radiation in the context of climate change and in the development of scientific collaboration with the NASA Aura satellite.

## INTRODUCTION

To address global climate change and large scale atmospheric change, an integrated strategy utilizing small satellites, *in situ* measurements, laboratory studies, and adaptive modeling is required. Probing the underlying feedback mechanisms demands excellent temporal resolution and wide spatial coverage, while monitoring the evolution of the chemical fields requires global vision. An integrated approach to the experimental requirements, combining satellite measurements and *in situ* studies, provides the only immediate, feasible solution to this problem. The requirements for these *in situ* measurements are clear; the suite of measurements must:

- monitor species required to validate remote measurements,
- monitor enough species simultaneously to provide complete context for modeling,
- cover sufficient range to initialize models,
- offer sufficient temporal resolution for mechanistic studies,
- map local and regional scale dynamics, and
- log sufficient flight hours to assess the validity of benchmark and surrogate variables.

With the new Altair uninhabited aerial vehicle (UAV), NASA has the unique capability to meet these needs and to usher in a new era of *in situ* atmospheric measurements. Only

NASA controls the technology required to address global climate questions with emerging small satellite, UAV, and miniaturized laser technologies. By leveraging new miniaturized technologies in electronics, detectors, and laser sources, many measurements may be made by a single payload; such a payload will provide NASA with a powerful tool for validating satellite measurements, initializing models, and probing feedback mechanisms. Moreover, this miniaturization will provide improved noise immunity, yielding laboratory quality measurements from an *in situ* platform.

The instrumentation aboard the Aura satellite will provide the atmospheric community with a wealth of new data for use in climate models to better monitor the health of the atmosphere, better quantify climate change, and better predict future climate states. However, these prognoses, results, and predictions can only be as credible as the models used for the forecast. To properly assess and improve these models, detailed *in situ* measurements are necessary because only these measurements can provide the crucial link between small scale phenomena and regional and global measurements, thereby tying cloud microphysics and structure to chemical fields to dynamic transport patterns.



## SCIENTIFIC OBJECTIVES

The Climate Change Science Program (CCSP) and the NASA Aura program have delineated the following questions:

1. How is atmospheric composition changing?
2. What trends in atmospheric constituents and solar radiation are driving global climate?
3. How do atmospheric trace constituents respond to and affect global environmental change?
4. What are the effects of global atmospheric chemical and climate changes on regional air quality?
5. What are the climate-relevant chemical, microphysical, and optical properties, and spatial and temporal distributions, of human-caused and naturally occurring aerosols?
6. What are the atmospheric sources and sinks of the greenhouse gases other than CO<sub>2</sub> and the implications for the Earth's energy balance?
7. What are the effects of regional pollution on the global atmosphere and the effects of global climate and chemical change on regional air quality and atmospheric chemical inputs to ecosystems?
8. What are the characteristics of the recovery of the stratospheric ozone layer in response to declining abundances of ozone-depleting gases and increasing abundances of greenhouse gases?
9. What are the couplings and feedback mechanisms among climate change, air pollution, and ozone layer depletion, and their relationship to the health of humans and ecosystems?
10. How will future changes in atmospheric composition affect ozone, climate, and global air quality?

The first six questions are addressed most directly with a combination of satellite measurements and aircraft-borne *in situ* measurements to provide the global context, validated benchmarks, and high spatial resolution necessary for detailed studies of composition, mechanism, and climate evolution. The next three mechanistic questions require very specific measurements with high time and spatial resolution to determine correlations between chemical fields that will elucidate the underlying mechanisms—such measurements can only be made from an *in situ* platform. The final question requires synergistic use of global data from remote measurements, mechanistic hypotheses from *in situ* data, a trusted model, and measurements designed to test that model so that the best possible climate predictions can be made based on the available data. We consider here the development of one of the key technologies, that of Integrated Cavity Output Spectroscopy (ICOS).

## DEVELOPMENT AND DEPLOYMENT OF THE INTEGRATED CAVITY OUTPUT SPECTROSCOPY (ICOS) TECHNIQUE FOR THE *IN SITU* DETECTION OF HDO AND H<sub>2</sub>O

We discuss here the airborne deployment of a new spectroscopic technique for *in situ* detection of rare atmospheric gases, funded by NASA's Instrument Incubator Program. This development effort was motivated by the scientific goal of measuring the isotopic composition of water vapor (the ratio HDO/H<sub>2</sub>O) in the near-tropopause region, where the mixing ratio of HDO is less than a part per billion. Because conventional spectroscopic techniques do not provide sufficient sensitivity to measure small changes in the isotopic ratio in this region, there is a need for new, more sensitive measurement techniques. The Harvard IIP work focused on the technique of Integrated Cavity Output Spectroscopy (ICOS). During the first two years of the IIP project, a bench instrument was constructed and the ICOS technique refined until its sensitivity reached the target for HDO science. In 2004, the laboratory bench instrument was converted into a fully autonomous flight instrument, integrated onto NASA's WB-57 aircraft, and flown in a series of test flights. These test flights demonstrated that laboratory ICOS performance could be reproduced in flight, with sensitivity levels exceeding those of most comparable spectroscopic instruments by more than an order of magnitude. The flights represented the first use of ICOS for *in situ* aircraft-borne atmospheric measurements. We review here the principles of ICOS, describe the instrument construction and attendant issues, and show data from the 2004/2005 test flights.

### INTEGRATED CAVITY OUTPUT SPECTROSCOPY (ICOS)

ICOS is an optical-cavity based absorption spectroscopy technique [1,2]. As in the conventional absorption spectroscopy techniques used in many aircraft instruments, light from a narrowband, tunable, continuous-wave laser is injected into a cell containing a gas sample and tuned across a spectral feature of the molecule of interest (Fig. 1).

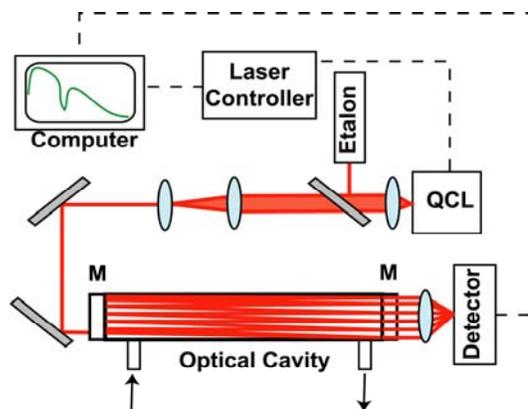


Fig. 1. ICOS schematic. Light from a mid-infrared cw quantum cascade laser is coupled into an optical cavity; output light is captured by an HgCdTe detector.

Light exiting the sample cell is captured on a detector; the resulting spectral signature gives the concentration of the absorbing molecules. For measuring molecular species at the part-per-billion level, conventional spectroscopic instruments typically use multipass cells that enhance absorption by increasing the optical pathlength through the gas sample. The upper limit for pathlength in these systems is on the order of 100 meters, i.e., approximately a hundred passes in a one-meter cell. ICOS overcomes this limitation by the use of a high-finesse optical cavity composed of highly-reflective mirrors rather than a multipass Herriot or White cell. With cavity mirrors of  $R = 99.98\%$  (200 ppm losses), photons entering the cell are trapped for nearly 5000 passes on average, producing an effective optical pathlength of nearly 4 km. For this reason the ICOS technique offered the promise of a 40 x improvement in sensitivity over conventional techniques extending detection thresholds to the part-per-trillion level. By winter 2003 our laboratory efforts had realized this promise, producing mid-IR spectra with noise comparable to that of conventional techniques but 40 x deep absorption features (Fig. 2). This performance allows the scientifically useful measurement of HDO/H<sub>2</sub>O ratios in the dry stratosphere.

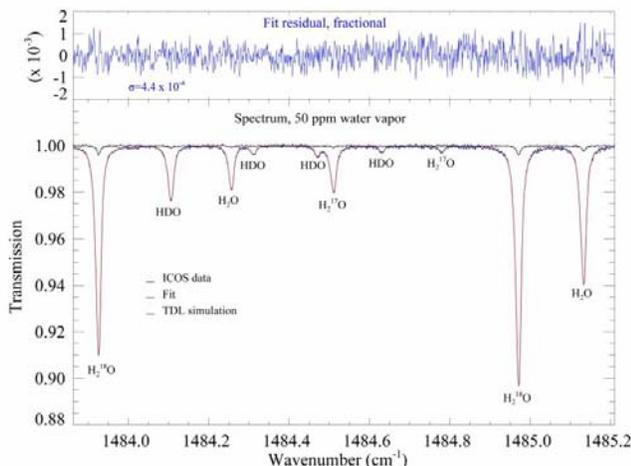


Fig. 2. Laboratory ICOS spectrum of the target region for detection of HDO and H<sub>2</sub>O, in blue, with the fit to the data overlaid in red. For comparison a synthetic representation of the signal from a conventional absorption instrument is shown in black. The increased absorption and corresponding sensitivity of the ICOS technique is readily apparent.

#### DESIGN OF THE FLIGHT SYSTEM

During 2004, the laboratory ICOS system was converted to a flight instrument for use on the WB-57 to establish in-flight performance. The conversion presented numerous challenges:

- *Optical cell and foreoptics*
  - The cell must be mechanically stable enough to maintain alignment even in hostile flight conditions
  - Cell flush rate must be less than 3 seconds to not compromise spatial resolution of data
- *Gas handling system*

- All inlet plumbing must be free of hysteresis: no trapped volumes, minimal surface adsorption
- *Thermal enclosure*
  - Temperature around optical system must be maintained to within several degrees.
  - Gradients across optical cell must be less than half a degree, because several of the absorption lines in the target spectrum are highly temperature-sensitive.
- *Calibration and fitting*
  - During flight, periodic calibration cycles must provide water-free baseline data to provide a power curve for fitting data.
  - Because flying a reliable water vapor standard is extremely difficult, calibration cycles require a calibration proxy.
  - Laser frequency and tuning characteristics must remain stable enough for reliable fits.
- *Electronics*
  - Operation of all systems must be fully autonomous and reliable.
  - Electrical noise must not compromise sensitivity.

Much of the work effort during 2004 was devoted to meeting these challenges. Elements of this work are briefly reviewed here.

#### OPTICAL CELL

Design of the optical cell required multiple considerations. The optical cell must provide a stable and noise-minimal optical alignment. It must also provide flow characteristics that minimize contamination. For robustness in flight, the optical cell was designed with no moveable parts or adjustment. Mirror position is determined only by the machining of the surfaces on which the mirrors rest, and all adjustments to optical alignment are provided by moveable mirrors in the foreoptics. This approach has not previously been attempted in laboratory cavity-based spectroscopy, where vibrations are readily controlled and external pressure changes are insignificant. We have found however that it works extremely well and provides a simple, reliable means of aligning the optical system in a flight system.

Because maximizing the free aperture of the mirror is vitally important to minimizing the “noise” of spurious cavity resonances, the cell is sealed with a radial o-ring around the mirror diameter rather than a standard face-seal on the mirror surface. This configuration allows us to make use of the full surface area of the mirror to spread out the beam pattern and minimize interferences between successive beam passes.

Optical cell design must minimize two potential avenues for contamination within the optical cell: (1) desorption of adsorbed water molecules from walls and surfaces, and (2) trapping of air and water from previous periods of the flight in stagnant air pockets in the cell. Surface adsorption was addressed by coating all surfaces exposed to measured gas with a Fluoropel, a hydrophobic fluoropolymer. Prevention of stagnant airspace required a larger design effort. Gas is

injected into both ends of the cell, near the mirrors, through four offset inlet ports at each end (Fig. 3). The offset ports provide a swirling flow that scours out the volume in front of each mirror and prevents development of a pocket of stagnant air (Fig. 4).



Fig. 3. Optical cell and gas handling plumbing for the Harvard ICOS instrument. Gas is injected from four ports around either mirror and exits from ports at cell center. Multiple exit ports are needed for symmetrical flow.

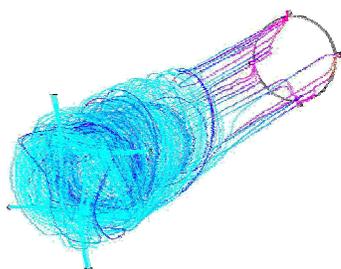


Fig. 4. Fluid-dynamics simulation of flow in one half of the ICOS optical cell. Color along each fluid parcel trajectory denotes time since injection. The offset injection ports produce a swirling flow that scours out the airspace in front of each mirror.

#### GAS HANDLING SYSTEM

The same contamination considerations for the optical cell apply to the tubing used to carry air to the optical cell: surface adsorption and dead volumes must be minimized. In the ICOS instrument, all gas-handling tubing is orbitally-welded, electropolished 1/2" diameter stainless steel tubing coated with Fluoropel. All connections on the input gas handling system are made with pharmaceutical-grade fittings (Swagelok VCO-B) that eliminate dead volumes.

#### THERMAL REGULATION

Temperature stability within the instrument was accomplished by enclosing the entire optical and calibration gas systems within an insulated and heated box, with 750 W of heat provided by thermofoil heaters mounted on the inner metal surface. Input air is thermally regulated by 75W of thermofoil heaters on the input tubing before the entrance into the thermal enclosure. This system was tested in the laboratory and proven to be adequate for heating input gas from the coldest ambient temperatures experienced (190 K) to the regulated enclosure temperature (298 K). Temperature

within the optical cell is monitored by two high-precision thermistors (0.1 K, 1 MOhm to prevent self-heating) mounted at cell center, at the waist of the beam pattern where they do not interfere with optical transmission. Temperature is also monitored along the cell via five matched high-precision thermistors mounted to the cell surface. Because tests in the laboratory show that the gas temperature gradient within the cell is a well-defined function of the temperature gradient along the cell surface, this allows monitoring and evaluation of any thermal inhomogeneities in the gas sample.

#### CALIBRATION AND FITTING

During periodic calibration cycles during the flight, the cell is flushed with ultradry air to allow measurement of a water-free baseline power curve for the laser. For this purpose we use research-grade nitrogen gas (Matheson) with water vapor mixing ratio guaranteed below 0.2 ppm, i.e., less than 5% of the minimum water vapor measured during flight. This residual water does not mean that the measurement is subject to 5% error: if the laser tuning characteristics remain stable, any residual baseline water can be corrected in the final data reduction by simple addition to the derived mixing ratio. Laser tuning characteristics are monitored continuously during the flight by splitting a small fraction of the laser power into a Ge etalon, which provides a measurement of laser frequency.

Calibration cycles also include several minutes of measurement of an in-flight calibration standard that serves as a proxy for water vapor. We have identified methyl fluoride ( $\text{CH}_3\text{F}$ ) as the best proxy, as it provides a series of strong and well-separated absorption lines over the instrument's target spectral region. As a non-polar molecule,  $\text{CH}_3\text{F}$  presents no danger of adsorption onto wall surfaces and contamination of subsequent measurements.

#### TEST FLIGHTS

The first test flights of the ICOS Isotope Instrument were made on the WB-57 out of Ellington Field in Houston, TX, on a campaign from Nov. 2004–Jan. 2005. The goal of these flights was to obtain an understanding of instrument performance, to demonstrate that laboratory sensitivity is maintained in flight, and to validate the instrument measurements. The need for validation mandated that the aircraft payload contain numerous instruments providing simultaneous measurements for comparison. For this reason the instrument payload included four independent measurement of  $\text{H}_2\text{O}$  and two of  $\text{HDO}$ . The total payload of the test flight series is described in Table 1 and shown in Fig. 5.

The two Lyman- $\alpha$  instruments are long-established, well-characterized and well-calibrated instruments that have participated in numerous NASA science missions. The  $\text{HO}_x$  isotope instrument is based on an established instrument (Harvard  $\text{HO}_x$ ) that is now modified for measurement of  $\text{H}_2\text{O}$  and  $\text{HDO}$ . Clouds and cirrus can be identified by comparing

the Lyman- $\alpha$  total water and water vapor instruments; this allows evaluation of any contamination of new instruments by evaporation of cloud ice particles. All instruments have a rapid data rate, allowing validation of their intrinsic response time, a critical concern when measuring the rapid fluctuations in water vapor concentrations expected in the near-tropopause region.

TABLE 1

Instrument	Gases	Phase	Integration time
ICOS	H <sub>2</sub> O, HDO, H <sub>2</sub> <sup>18</sup> O, H <sub>2</sub> <sup>17</sup> O, CH <sub>4</sub>	gas phase	3 s
Hoxotope	H <sub>2</sub> O, HDO	gas phase	12 s
Lyman- $\alpha$ Water Vapor	H <sub>2</sub> O	gas phase	3 s
Lyman- $\alpha$ Total Water	H <sub>2</sub> O	combined gas phase + condensate	3 s

In order to test the instruments most fully, flight plans were designed to probe the instruments' dynamic range, response time, sensitivity, and robustness to contamination. The WB-57 flew flight legs at a variety of altitudes from mid-troposphere to stratosphere, with water vapor mixing ratios varying from many hundred ppm to less than 5 ppm. During some sections of the flights, pilots were instructed to maintain level altitude in cloud-free air to provide relatively constant mixing ratios and the clearest possible comparison of the different instruments' retrievals; this allows identification of any systematic errors. At other times, pilots made transects through cloud tops and near-tropopause cirrus wherever possible to test the instruments' imperviousness to evaporation of cloud particles. Sharp cloud boundaries also provided a test of the instruments' intrinsic response times. Ascents and descents provided a test of the instruments' performance under conditions of differing external pressure.



Fig. 5. The total payload for the Harvard isotope test flights of November 2004–January 2005.

## RESULTS

All subsystems of the ICOS instrument performed well during the test flight series. The electronics proved relatively trouble-free, with no additional sources of noise during flight. Temperature and pressure were well controlled. Temperatures in the optical system were regulated to a few degrees K during the entirety of the flight, and temperature gradients along the optical cell were less than the identified 0.5 K limit. Pressure within the cell was regulated to less than 0.3 torr for the bulk of the flight. Cell pressure was allowed to vary at the highest flight altitudes (i.e., lowest ambient pressure, < 60 torr) but even in this case data proved relatively easy to fit and measurement accuracy was not compromised. This stability produced instrument sensitivity at near-laboratory values, giving measurement precision for HDO of 60 ppt even in the dry stratosphere, sufficient for addressing all identified science issues involving HDO/H<sub>2</sub>O in the near-tropopause region.

Hysteresis and contamination due to variations in atmospheric water were also shown to be minimal during the test flights. Fig. 6 shows water vapor measurements from all four instruments during the flight of Jan. 11, 2005; all four instruments track the same atmospheric features, with no identifiable lags. Fig. 7 narrows in one portion of the flight, in which the airplane flew a level flight leg at 9 km through heavy cirrus and then ascended into the dry stratosphere. Water vapor concentrations change abruptly from several hundred ppm (with total water > 500 ppm) to stratospheric values of 5 ppm. The ICOS measurement shows no detectable contamination or lag during this transition. These results demonstrate that the instrument is capable of making uncontaminated measurements even during quite wide swings in ambient atmospheric water concentrations.

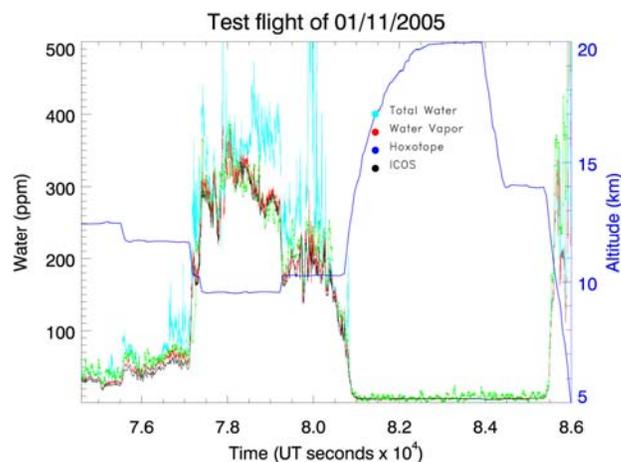


Fig. 6. Water vapor measurements by four independent instruments during the test flight of Jan. 11, 2005. The total water instrument is shown in light blue; this trace exceeds the others during crossings through clouds or cirrus. All instruments reproduce the same features over a large dynamic range. Note that ICOS precision for measurement of water vapor already exceeds that of the Lyman- $\alpha$  instruments.

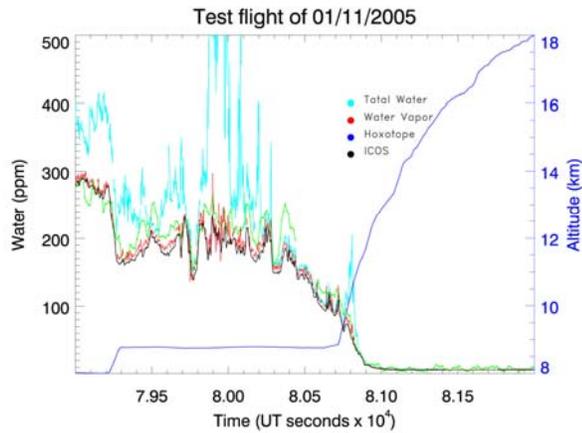


Fig. 7. A subsection of the Jan. 11 flight, in which the aircraft climbs abruptly from 9 km, within the troposphere, into the dry overworld stratosphere. Neither of the isotope instruments shows residual contamination from the recent transect through cirrus containing over 500 ppm total water.

## CONCLUSIONS

During 2004, we proved the effectiveness of the ICOS technique and made the first demonstration of its usefulness for *in situ* gas measurement from an aircraft. We completed, integrated, and test-flew a new instrument that can serve as a valuable addition to NASA research payloads for years to come. We provided new measurements of HDO and H<sub>2</sub>O that show interesting and previously unobserved physical phenomena. The instrument promises to provide a valuable science contribution to NASA research missions, especially with regard to planned missions to the tropics, where ICOS HDO measurements can be used to explore questions of troposphere-stratosphere exchange and the origin of stratospheric water vapor.

## REFERENCES

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