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OUTLINE

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Future Directions of Stable Isotopic Ratio Infrared Spectrometry (SIRIS)

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- Motivation for SIRIS measurements
- Critical Requirements for IRIS Techniques
- Examples of IRIS Applications
  - NCAR Mid-Infrared DFG based CO_2 Isotopic Ratio Spectrometer: Current Status
  - NASA Mid and Near Infrared SIRIS instrumentation Needs
  - Industrial: Aerodyne, Physical Sciences, Picarro, Wagner
- General Discussions
- Conclusions

Future Directions of Stable Isotopic Ratio Infrared Spectrometry

- IRIS Applications
  - Atmospheric and planetary sciences
    - Environmental monitoring
  - Medical & Pharmaceutical
  - Geochemistry
- Targeted isotopic species
  - Water , CO_2, CH_4, N_2O, CO
- Infrared Spectrometry
  - Optical Enhancement Techniques
  - Infrared Spectroscopic Sources and Detectors
  - Advanced Pre-Concentrator Technology

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E.Kerstel, Chpt 34:Infrared ratio Infrared Spectrometry in Handbook of Stable Isotopes Analytical Techniques (2003)

Critical Subsystems for IRIS

- **Spectroscopic sources**
  - Near infrared diode lasers
  - Lead salt diode lasers
  - Quantum and Interband cascade lasers
  - Nonlinear Frequency Conversion (DFG, OPO)
  - Solid state lasers
- **Enhancement Techniques**
  - Absorption spectroscopy (WMS)
  - Photoacoustic spectroscopy
  - Cavity enhanced spectroscopy
  - NICE – OHMES

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Primary requirement for IRIS techniques

- Sensitivity 0.01% - 10^{-6} levels (precision accuracy)
- Selectivity
- Rapid response time
- Autonomous, unattended, remote operation and control
- Self calibrating
- Cost of ownership
- Low weight, small size, low power consumption
- Easy to use (avoid complexity)

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IRIS System Considerations

- Design and Architecture (COTS based system)
- Precision and Accuracy (Temperature, Pressure and Humidity
- Inlet design
  - Gas sampling (local-remote)
  - Filtering and pre-concentration
  - Calibration
- Data acquisition and signal processing
  - Ethernet and GPS option
- Intercomparison with IRMS and FTIR (0.01 – 0.05% range)

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Motivation

- Study of the Carbon Cycle: Land, Ocean, Atmosphere
- Combustion of fossil fuels increase atmospheric CO_2 levels and in turn global temperatures
- Currently, oceanic and terrestrial biospheres absorb 50% of anthropogenic atmospheric carbon. Will the sinks cease to take up CO_2 ?

- Major sources and sinks have been identified, but their specific mechanisms are still unclear
- Flexible and real time sensor is needed.
- Bring the instrument to the sample: Land, sea, troposphere, stratosphere, planets !

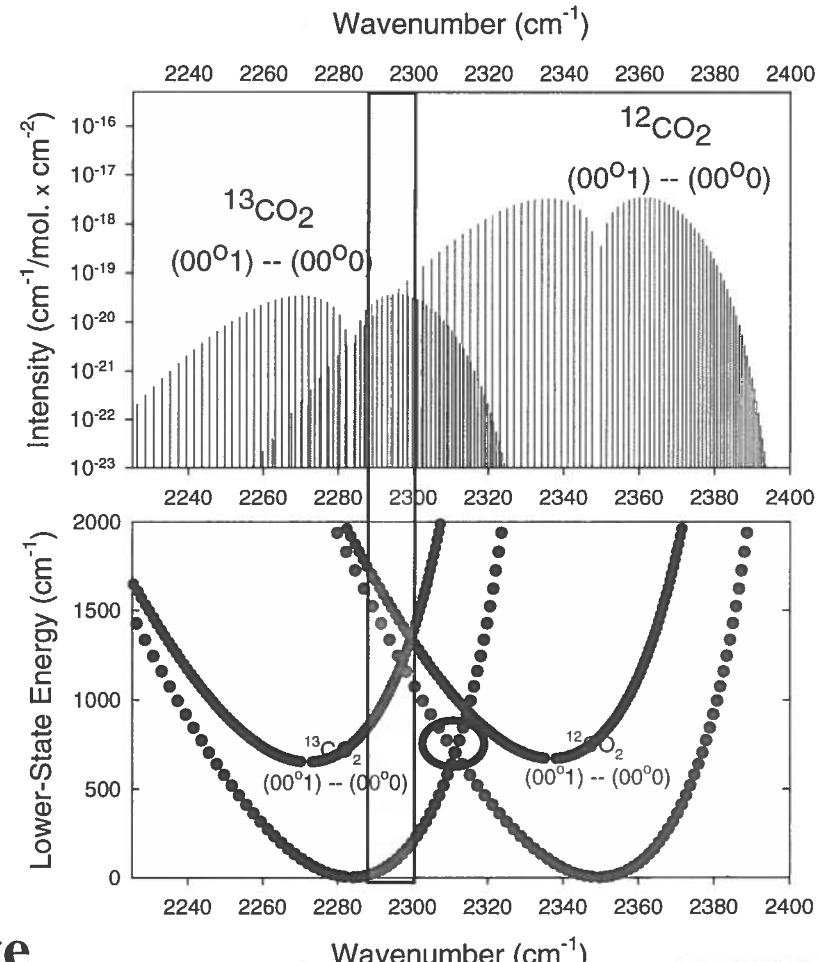
NCAR C-130

Accurate measurements of $^{12/13}CO_2$ ratios and other trace gases are key to attain detailed knowledge on carbon cycle processes

Equal Strengths or Equal Lower-State Energies?

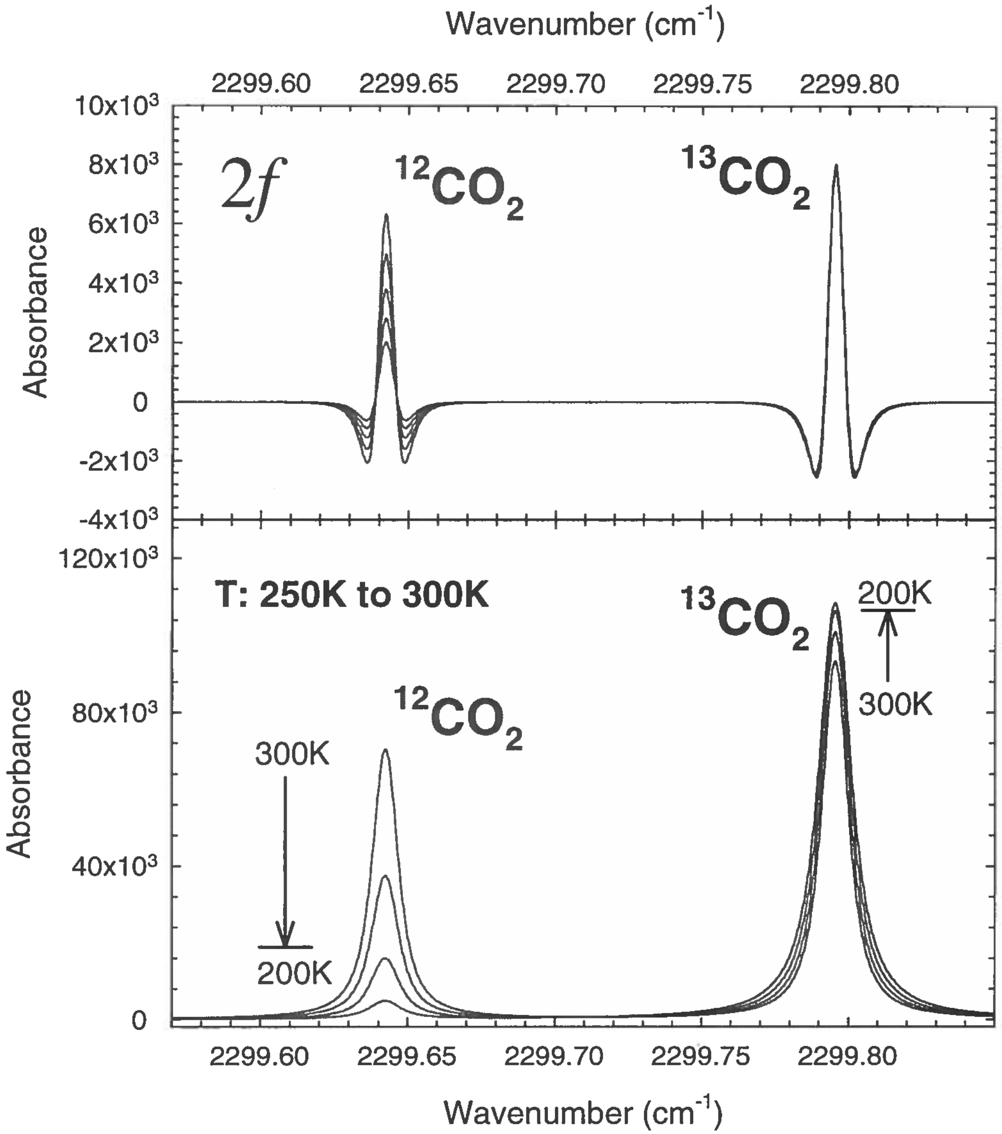
Most preferred method is balanced detection with isotopic lines of near equal lower-state energies (LSE)

- Achieved best precisions for laser spectroscopy reported to date, ~0.02‰ (Uehara et. al. 2002)
- Requires varying optical pathlengths to balance line absorption strengths (e.g. 1m and 100m)
- Disadvantages:
  - Achieving 100-meters requires large volume
  - Expensive and difficult to operate a separate reference cell of known $^{13/12}CO_2$ precision with dual pathlengths



We will use equal lines to investigate the advantages of such an approach

Temperature Dependence of Equal Line Strengths



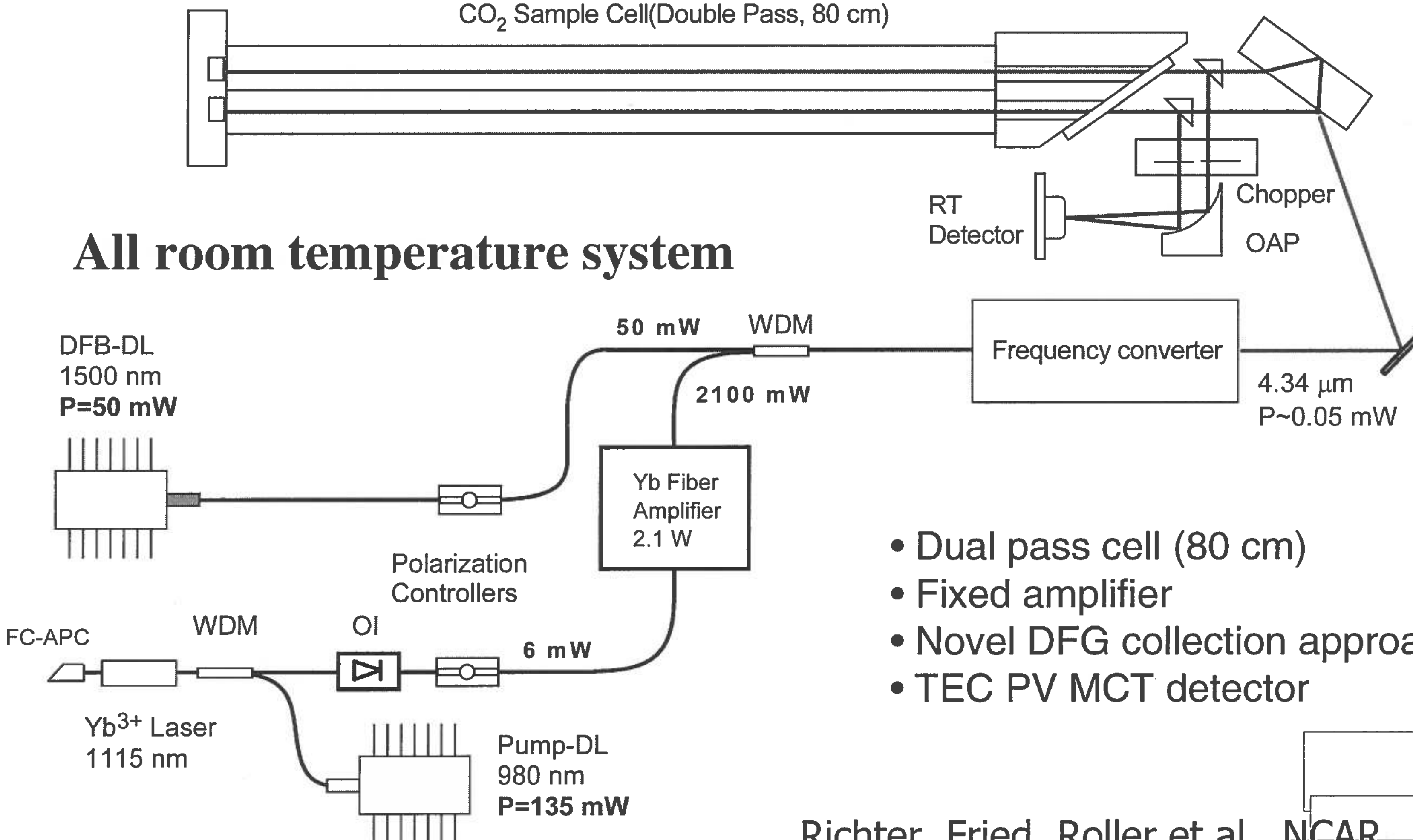
Beer's Law

$$I = I_0 e^{-\alpha.c.L}$$

$$\Delta T = \frac{\Delta \delta \; kT^2}{\Delta E}$$

$\Delta\delta^{13}$		ΔT
0.1°/oo	-->	6 mK
0.05°/oo	-->	3 mK

NCAR Mid-IR Isotopic Ratio Spectrometer



All room temperature system

- Dual pass cell (80 cm)
- Fixed amplifier
- Novel DFG collection approach
- TEC PV MCT detector

Richter, Fried, Roller et al., NCAR,
Boulder, CO, Aug. 2004

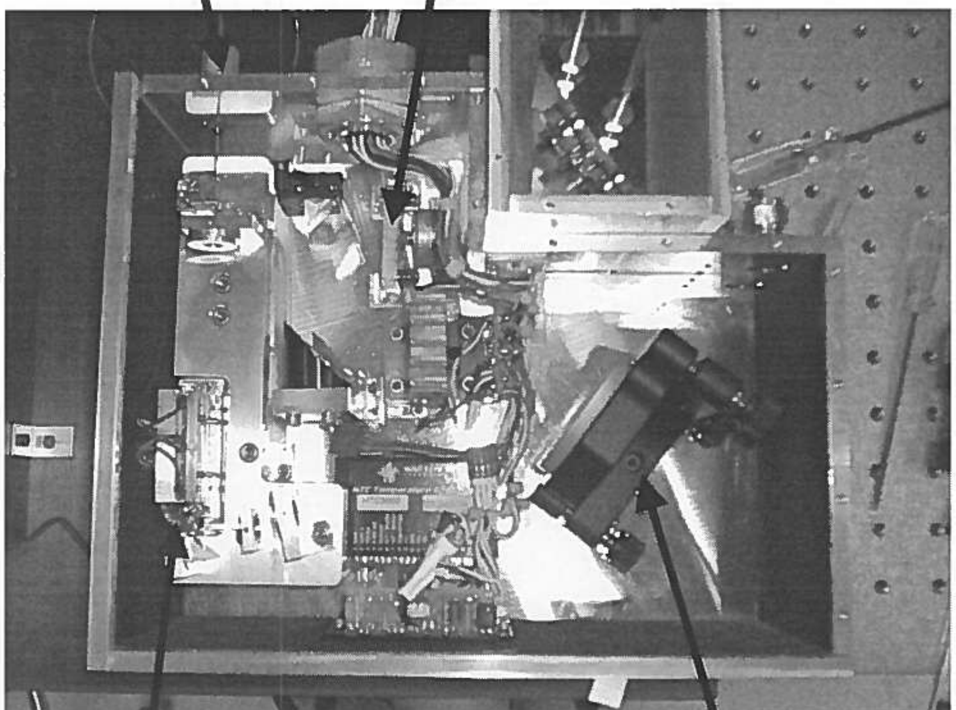
Current DFG based IRS System

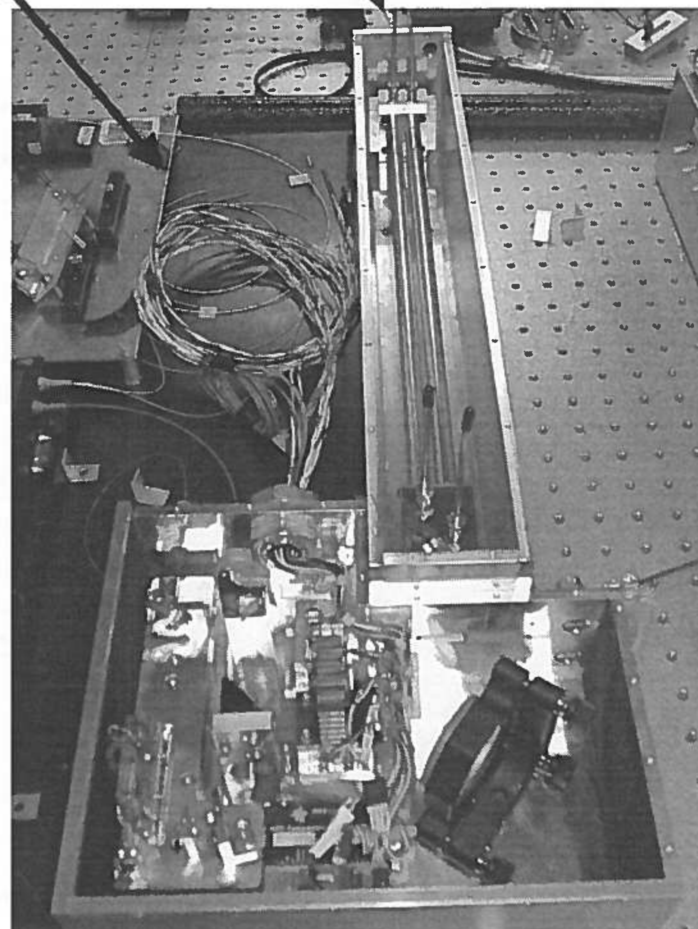
Fiber Entry

Chopper

Light Weight
Carbon Fiber
Bench

Dual Cells





PPLN Crystal

Beam Splitter

Conclusions

- DFG is a possible approach to $^{13/12}CO_2$ measurements of CO2 absorption features of near equal intensities
- The DFG system is liquid-N_2 free
- Balanced line strengths, while sensitive to temperature, offers more flexible gas sampling
- Also provides identical optical baseline background
- Analysis of lines shows a strong temperature dependence on per-mil precisions
- What's next: Perform measurements with new DFG system and absorption cell to assess performance and issues

NASA Mid-IR and Near-IR in situ Instrumentation Needs

- Atmospheric and Planetary Sciences
  - Global CO_2 mapping in near-IR at 1.57 μm (30012<-00001) band and 2.05 μm (30013<-00001) band as well as in the 4.3 μm ν_3 fundamental band
  - Environmental monitoring
  - Climate monitoring and diagnostics (carbon cycle greenhouse gases)
- Astronaut Habitat Environmental Monitoring
  - Fire detection and control
  - Air quality in spacecraft habitats

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