RQI Colloquium, Aug 22, 1997

Comparison of FTIR and Diode Laser Based Spectroscopy for Trace Gas Detection

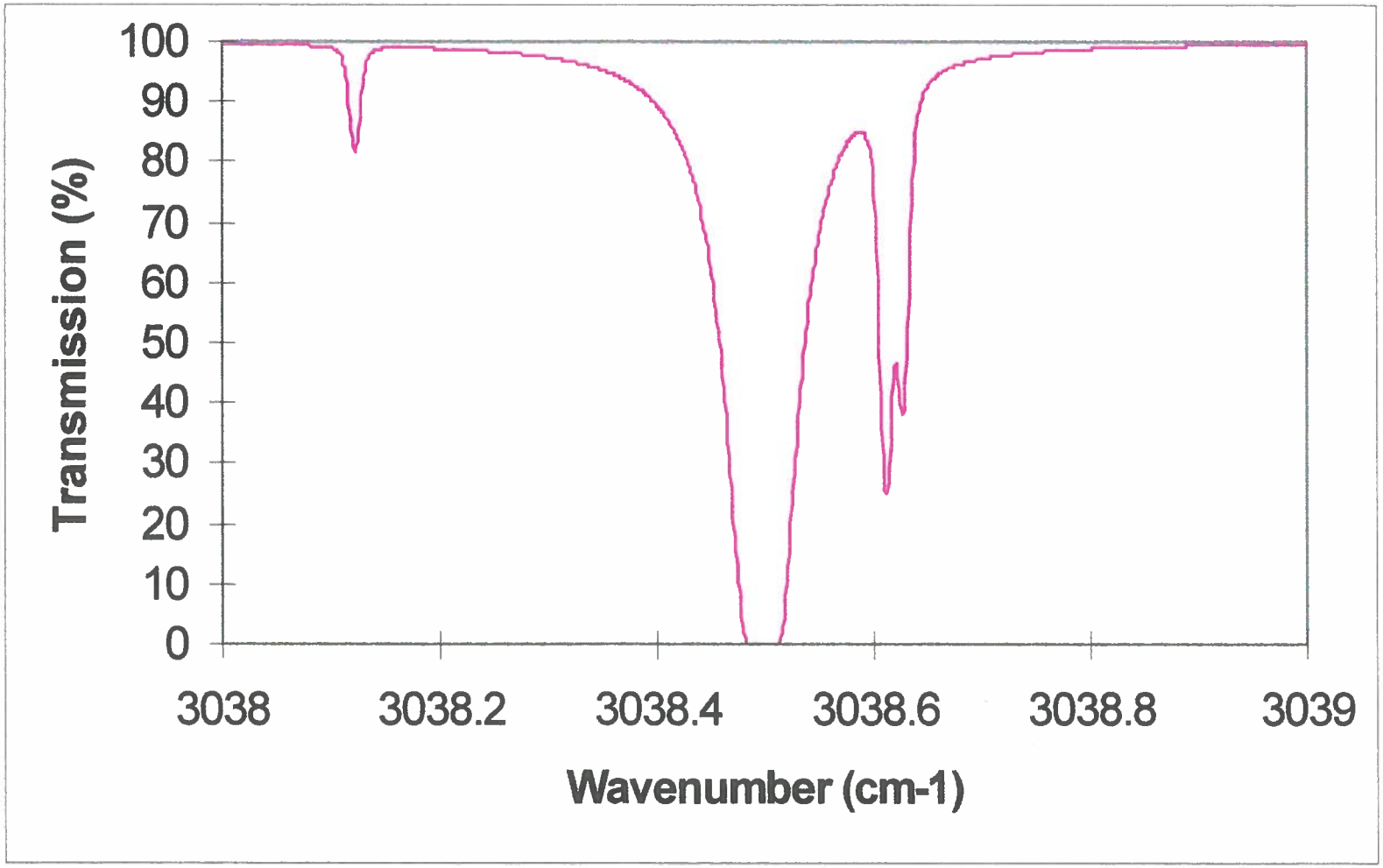
D. Moinet, K.P. Petrov, R.F. Curl, F.K. Tittel
Department of Electrical and Computer Engineering
Rice University

Motivation

- Why detect methane
  - Pollutant gas, EPA exposure limit
  - NOAA : Study of carbon cycle
  - NASA : detection of methane flux from rice based agroecosystems

- Selection of optimum absorption line
  - Absorption line at ν = 3038.5 cm-1 (λ = 3.29 μm)
  - Line is not interfered by H_2O or CO_2 in ambient air
    - ➡ Lorentzian profile
  - Isolated spectral line is of interest for laser spectroscopy
  - Line strength sufficient for detection : S = 8.92. 10-20 cm/mol
  - Readily accessible by mid-infrared sensor

GEISA Methane absorption line at 3038.5 cm^{-1} (30 torr pure methane)



FTIR Technique

- Necessity of a "background spectrum" (no sample in the beam) which is indicative of instrumental and environmental contribution to IR spectrum.
- Transmittance spectrum : $\%T = I / I_o$
  - I : Intensity measured with sample in beam
  - I_o : Intensity from background spectrum
- Absorbance spectrum $A = - \log_{10} T$

- FTIR parameters for improving SNR
  - SNR α Resolution
  - SNR α $(N)^{1/2}$ N : Number of scans
  - SNR α $(T)^{1/2}$ T : Acquisition time

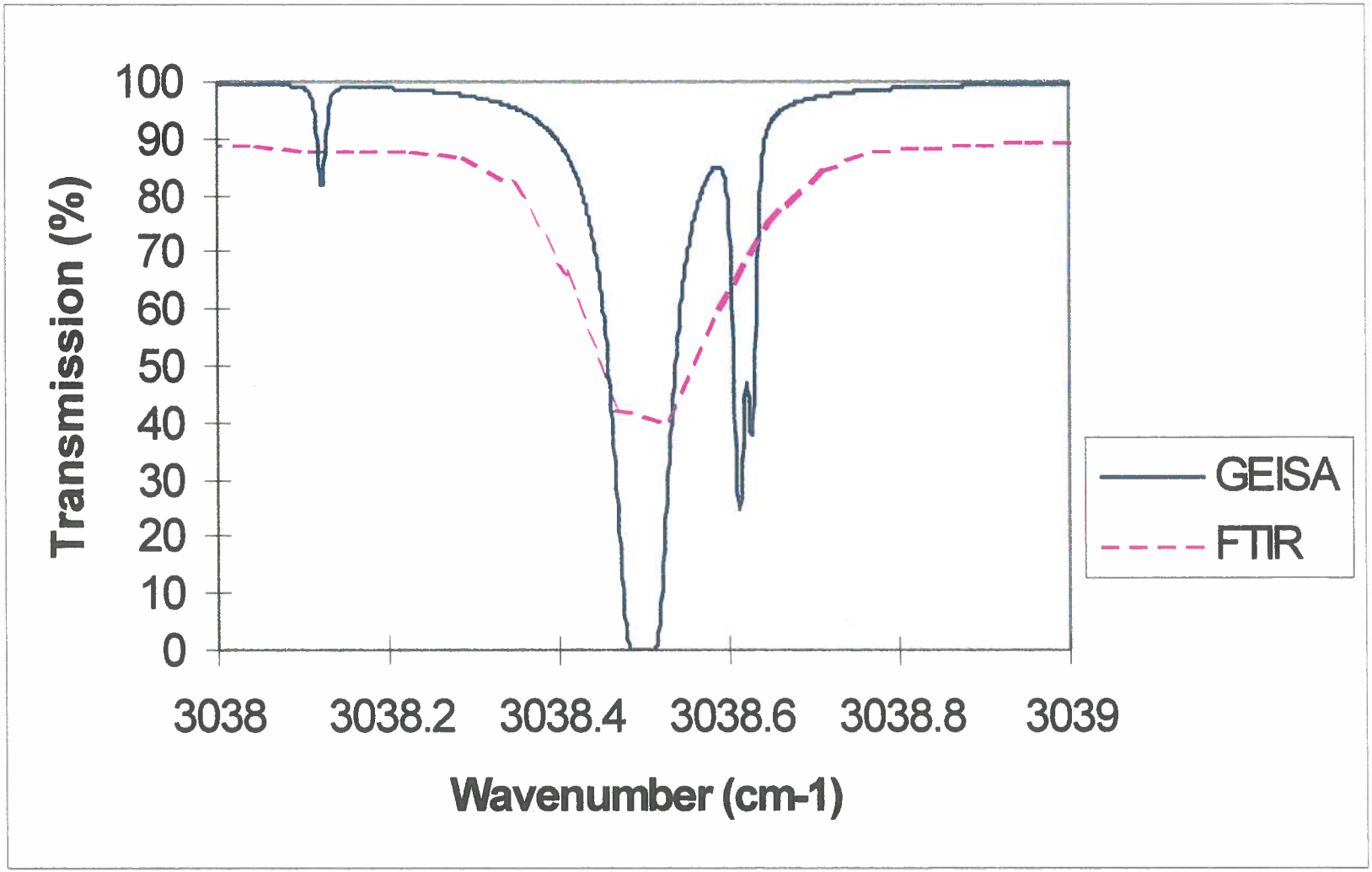
⇒ High resolution spectra are noisier than low resolution spectra

⇒ To increase SNR, an increased number of scans is necessary leading to a longer acquisition time

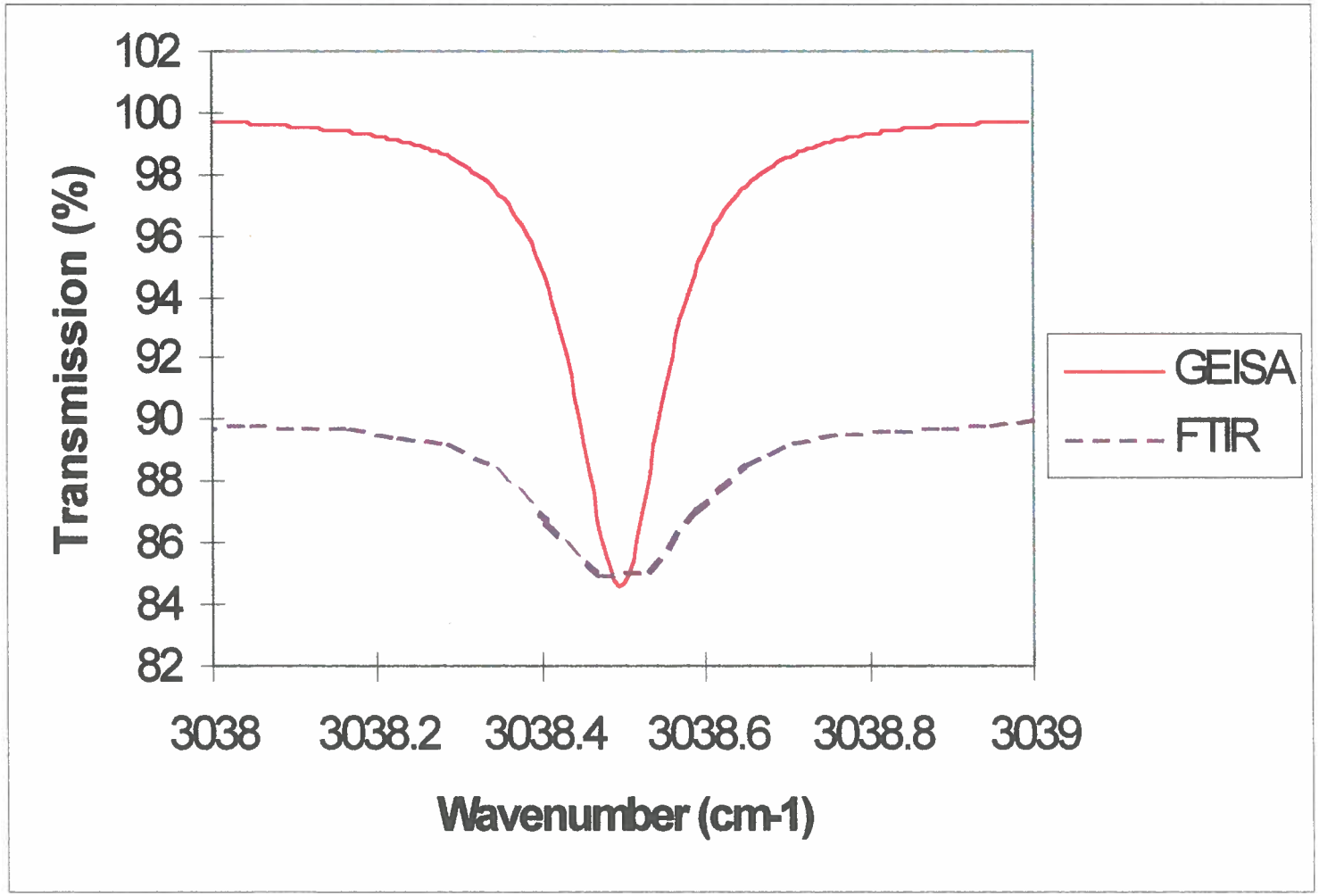
FTIR Experiment

- Nicolet MAGNA IR 760 Spectrometer
  - Spectral coverage : 400 - 4000 cm^{-1}
  - Resolution : 0.125 - 32 cm^{-1}
  - Minimum absorbance detectable: 10^{-4} - 10^{-5}
  - Weight : 100 lbs (vol = 0.5 m^3)
  - Price : $ 75k
- Experimental conditions
  - Resolution : R = 0.125 cm^{-1}
  - Number of scans : N = 100
  - Acquisition time : T = 30 mn
  - Signal to Noise Ratio : SNR = 30
- Absorption cell
  - Length : L = 15 cm to fit the spectrometer optical bench
  - Windows : D = 38.1 mm
  - Material - Windows : CaF
    - Body : glass

FTIR of 30 torr pure methane



FTIR 3 torr pure Methane in 760 torr air

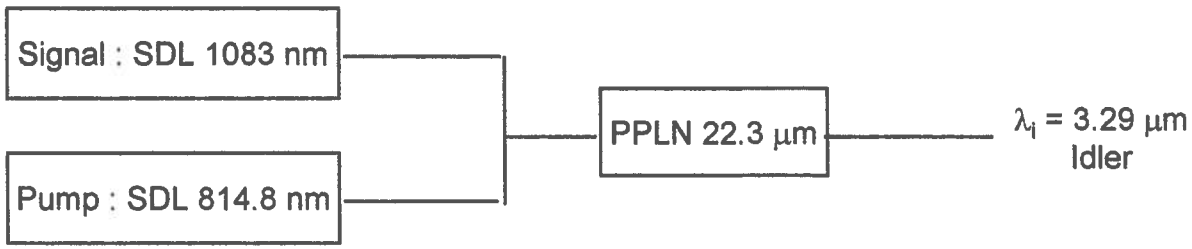


DFG Technique

- DFG pump source requirement
  - Methane absorption line : $\nu = 3038.5\ cm^{-1}$, $\lambda_i = 3.29\ \mu m$
  - DFB Laser diode source : $\lambda_s = 1083\ nm$
  - Phase matching condition : $k_p = k_s + k_i$ ⇒ $\lambda_p = 814.8\ nm$
- PPLN crystal
  - Quasi-phase matching condition ⇒ Λ : Grating period

$$\Lambda = \frac{2\pi}{k_p - k_s - k_i} = \frac{1}{\frac{n_p}{\lambda_p} - \frac{n_s}{\lambda_s} - \frac{n_i}{\lambda_i}} = 22.3\ \mu m$$

  - Crystal with multiple grating periods from 21.5 to 22.4 with increments of 0.1 μm is convenient



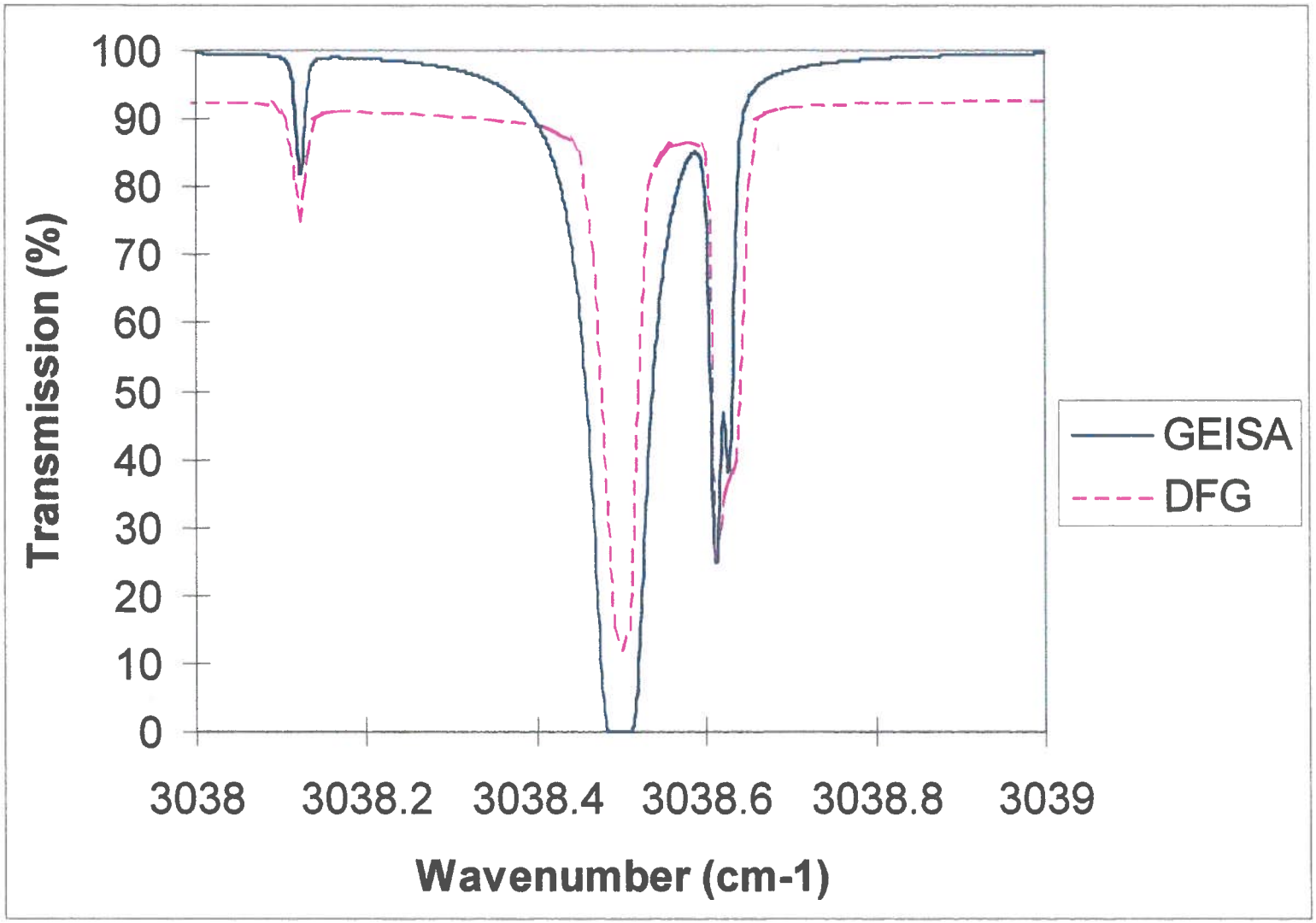
DFG Experiment

- DFG setup
  - Spectral coverage : 1 cm^{-1} , limited, target specific
  - Resolution : 0.5 - 20 Mhz
  - Minimum absorbance : 10^{-6}
  - Weight : 50 lbs (vol : 0.005 m^3) , semi-portable
  - Price : $ 50k

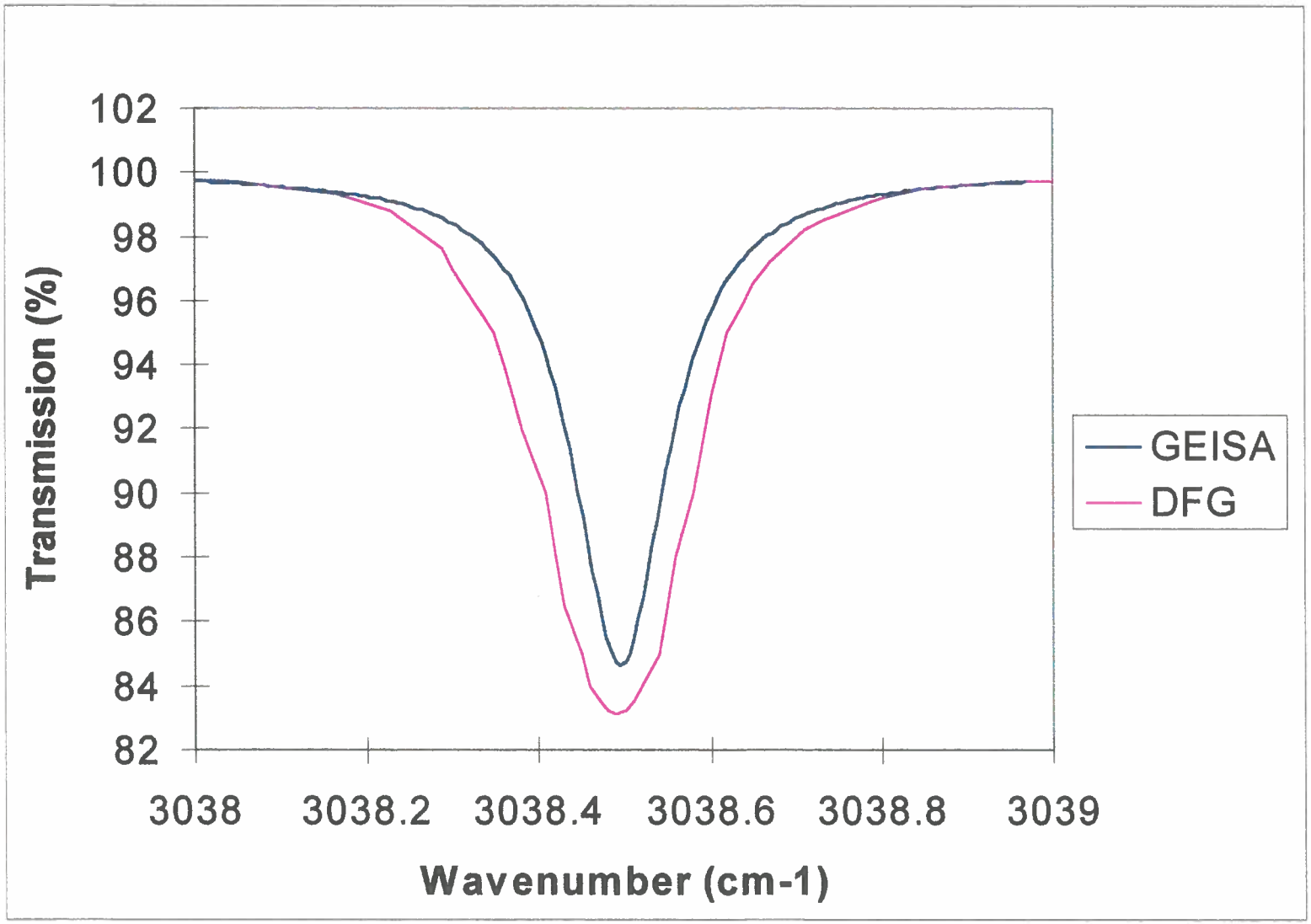
- Experimental conditions
  - Number of sweeps : 10 to 1000
  - Acquisition time : T = 0.1 sec
  - Signal to Noise Ratio : SNR = 300

- Absorption cell
  - Same as for FTIR experiment

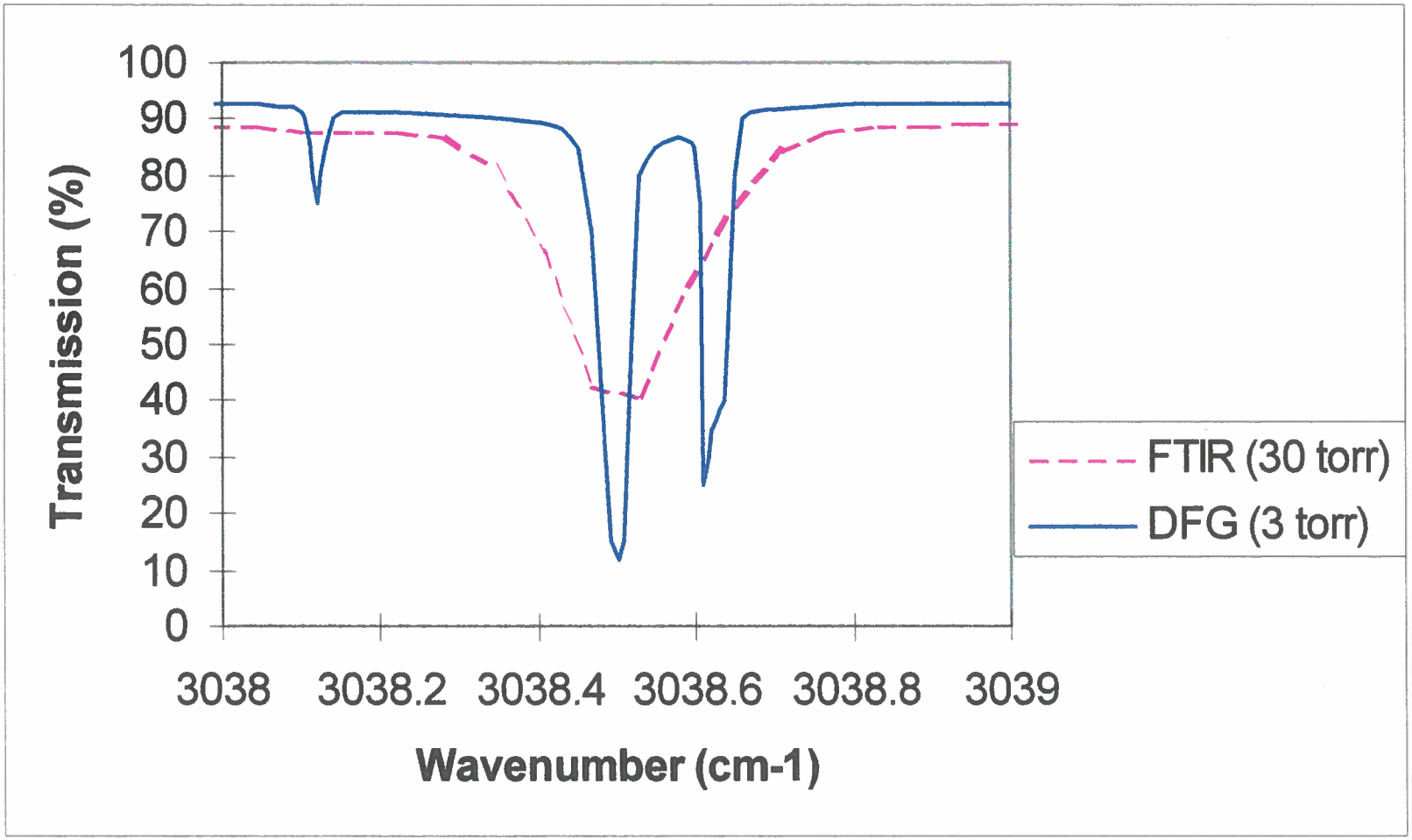
DFG of 3 torr pure methane



DFG of 3 torr pure methane in 760 torr air



DFG vs FTIR at low pressure



Comparison of DFG and FTIR characteristics

	FTIR spectrometer	DFG based sensor
Spectral coverage	Typically, 400 - 4000 cm^{-1}	Target specified, 1 cm^{-1}
Resolution	0.125 to 32 cm^{-1}	0.5 Mhz - 20 MHz
Minimum absorbance detectable	10^{-4} - 10^{-5}	10^{-6}
Acquisition time	Minutes	0.1 sec
Power consumption	60 W	50 W
Instrument dimension and weight	0.5 m^3 ; 110 lbs	0.05 m^3 ; 50 lbs
Price	75 k$	50 k$