Tunable Lasers and Wavelength Conversions: From Fundamentals to Applications

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Outline

* Motivation and Main Concepts
* Novel IR Laser Spectrometer
* High Resolution Molecular Spectroscopy
* Advanced Difference-Frequency Spectroscopic Sources
* Future Prospects

Advantages of Infrared Spectroscopy

* Nearly Universal Detector
  (Only homonuclear diatomics excluded)
* Characteristic Group Frequencies
* Ability to Distinguish Structural Isomers
  (Not necessarily true of mass spectrometry)
* Ability to Do *in situ* Non-Intrusive Probing
* Time Resolved Studies Convenient

Applications Where IR Laser Spectroscopies Excel

* ✳ Time Resolved Studies of Transients (Laboratory)
* ✳ Remote Sensing of Specific Chemical Species (Emissions)
    * Chemical plants and refineries
    * Automobiles
    * Rice fields
    * Forest fires
    * Volcanoes

Tunable CW IR Laser Sources

* **Color Center Lasers**
  Tunable (1-4 μm)
  Low temperature needed

* **Lead Salt Diode Lasers**
  Tunable (3-30 μm)
  Each diode $\sim 100\ cm^{-1}$
  Undesirable discontinuities
  Low temperature needed

* **Tunable III-V Semiconductor Diode Lasers**

* **CO and CO_2 Sideband Lasers**

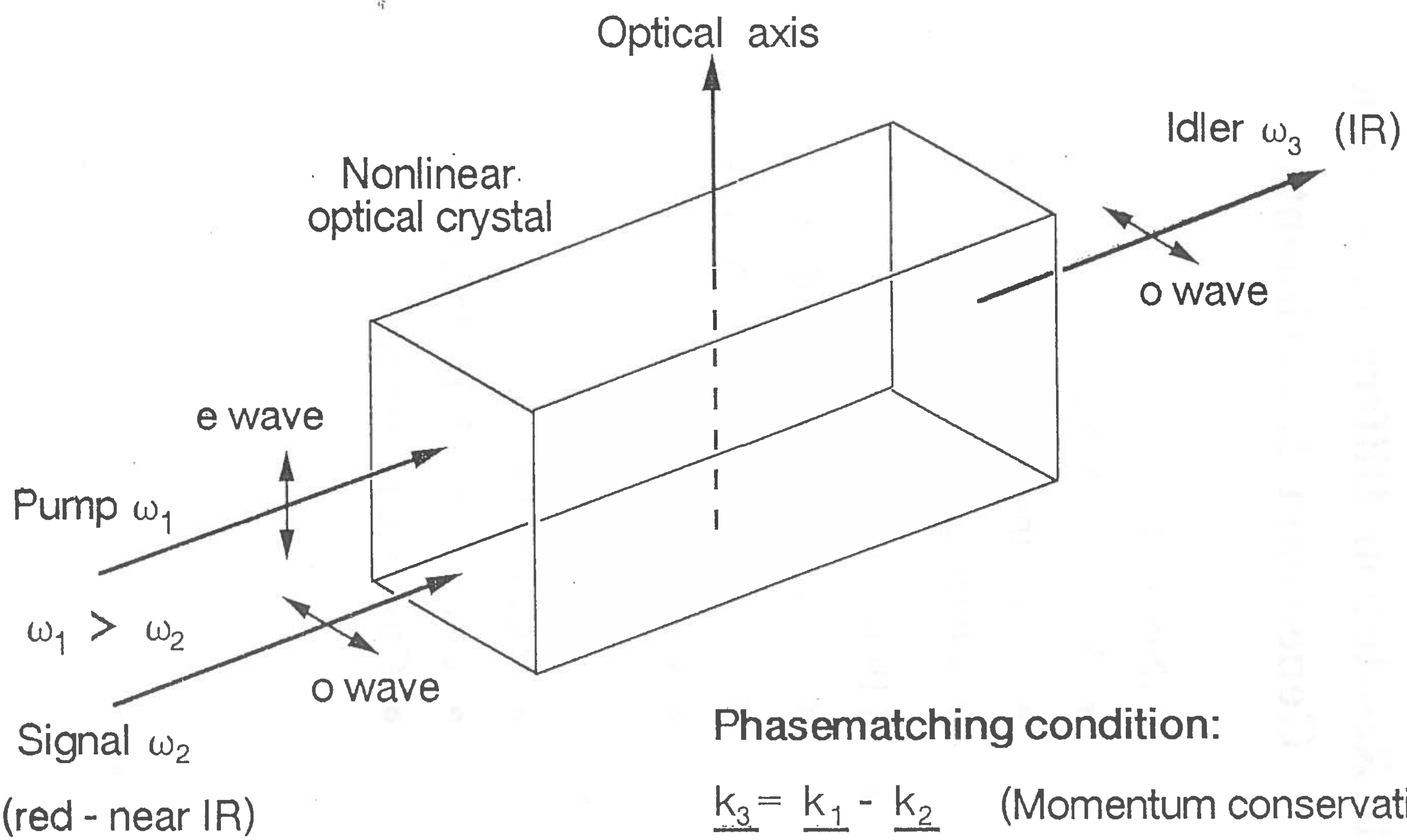
* **Difference Frequency Generation (DFG)**
  Tunable: 2-4 μm ($LiNbO_3$), 3-9 μm ($AgGaS_2$)
  Room Temperature

* **Optical Parametric Oscillators (OPO)**
  Tunable 2-4 μm ($LiNbO_3$, KTP, BBO)
  CW and Pulsed

High Resolution Difference Frequency Generation Experiments

- $LiNbO_3$ (1974)
  - A. Pine at NIST
  - Single mode Ar^+ and dye laser
  - Coverage to 4 µm
- $LiIO_3$ (1980)
  - T. Oka at University of Chicago
  - Single mode Ar^+ and dye laser
  - Coverage to 5.2 µm
- $AgGaS_2$ (1991)
  - Rice Group
  - 2 tunable single mode lasers
  - Coverage to 10 µm

Difference Frequency Generation (DFG)



Phasematching condition:

$\underline{k_3} = \underline{k_1} - \underline{k_2}$ (Momentum conservation)

$\omega_3 = \omega_1 - \omega_2$ (Energy conservation)

DFG Power

Assumptions :
- Gaussian beams
- lossless crystal
- phase matching
- $\rho = 0$

$$P_i = \frac{2\,\omega_i^2 k_s d_{eff}^2 l}{\varepsilon_o n_i n_p n_s c^3 (1+\mu)} P_p P_s h(\xi, \mu)$$

where $\mu = \frac{k_p}{k_s}$, $\xi = \frac{l}{b}$, $b = w_o^2 k$ and $h(\xi, \mu)$ is the focusing function.

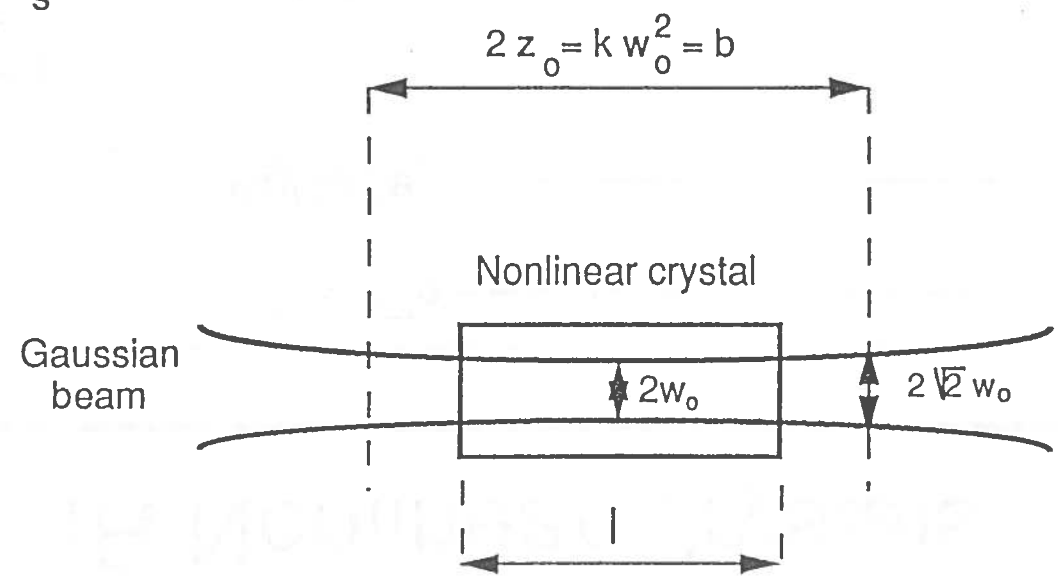
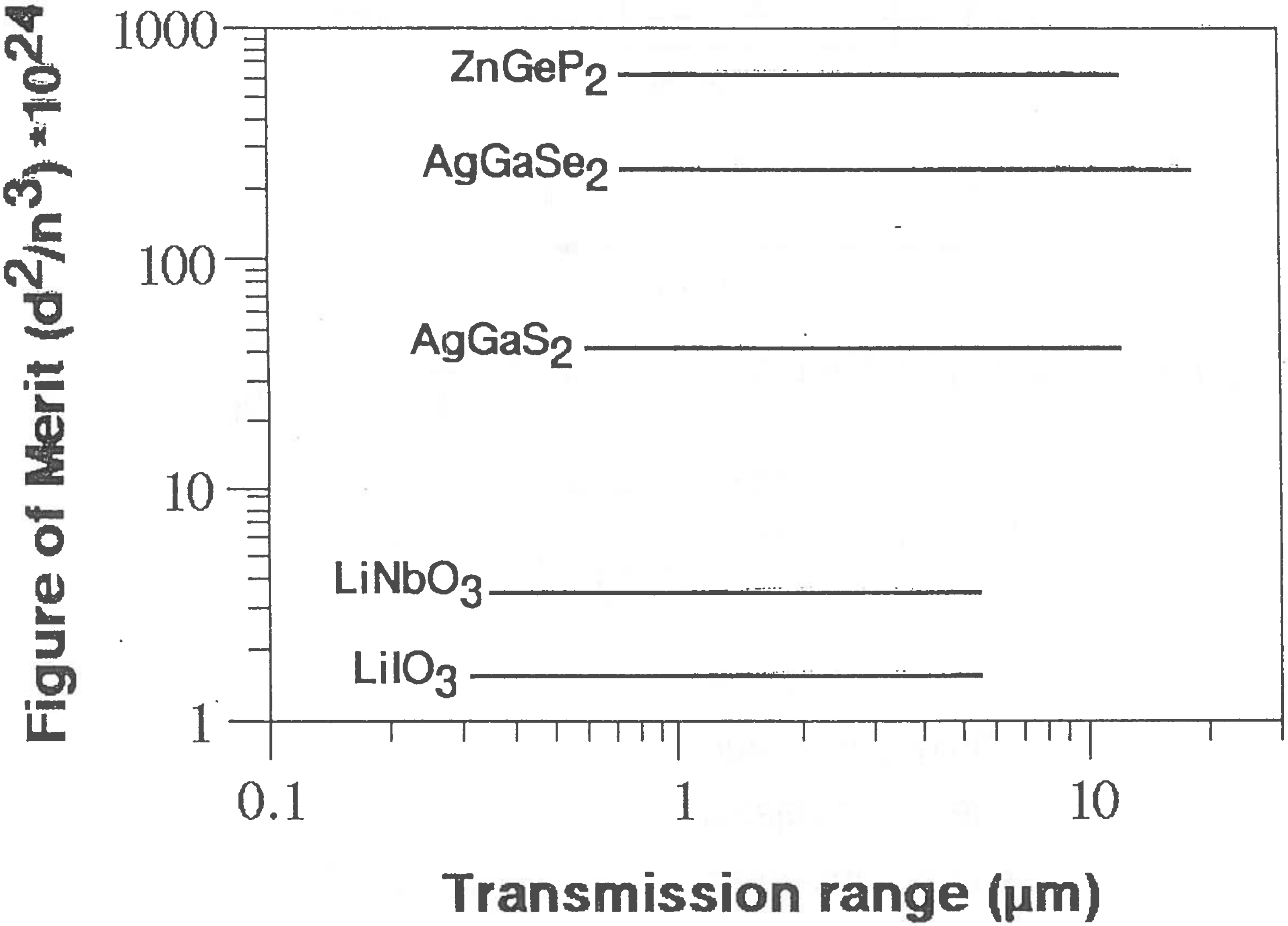


Figure of Merit for Various IR Nonlinear Crystals



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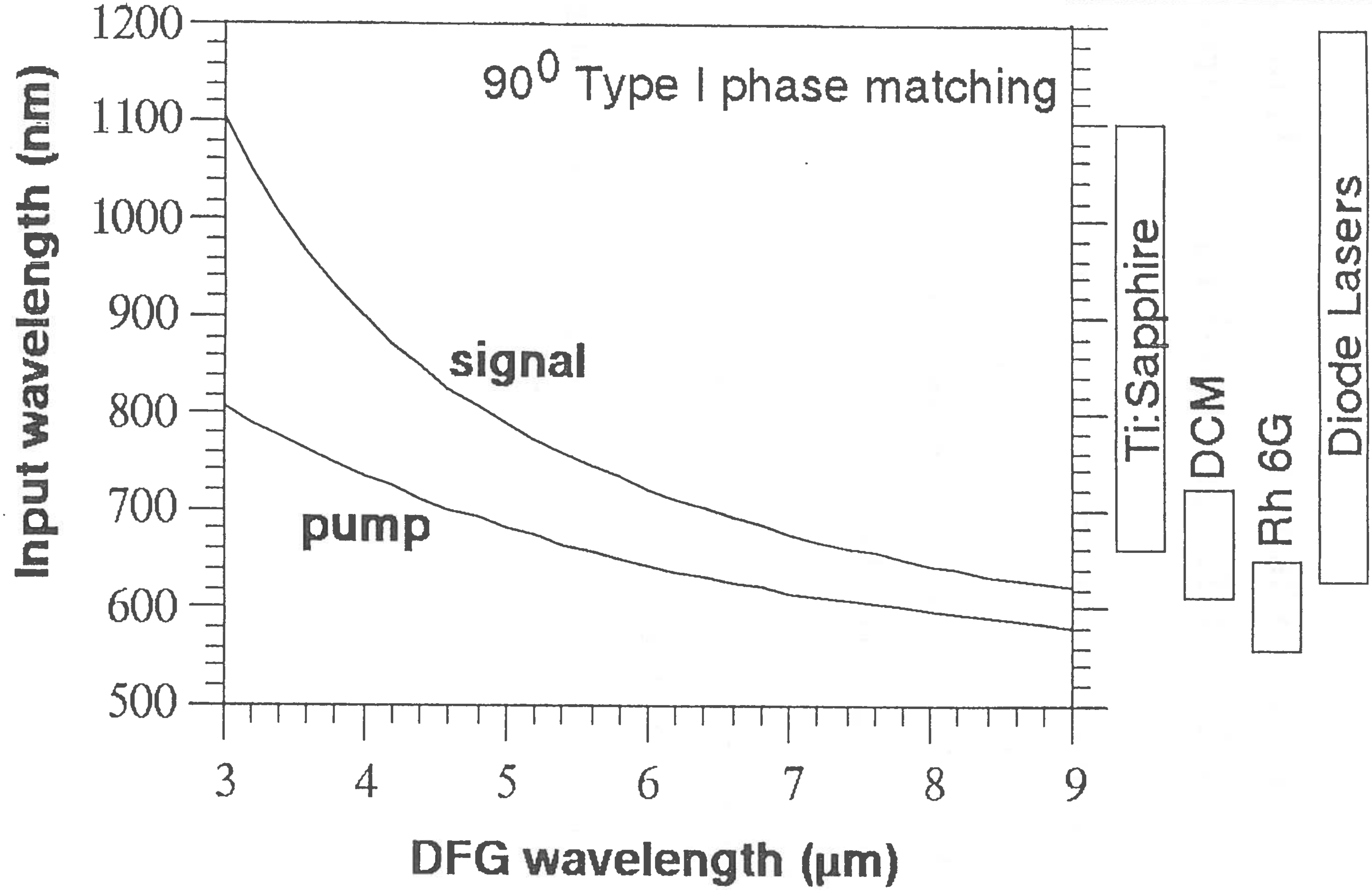
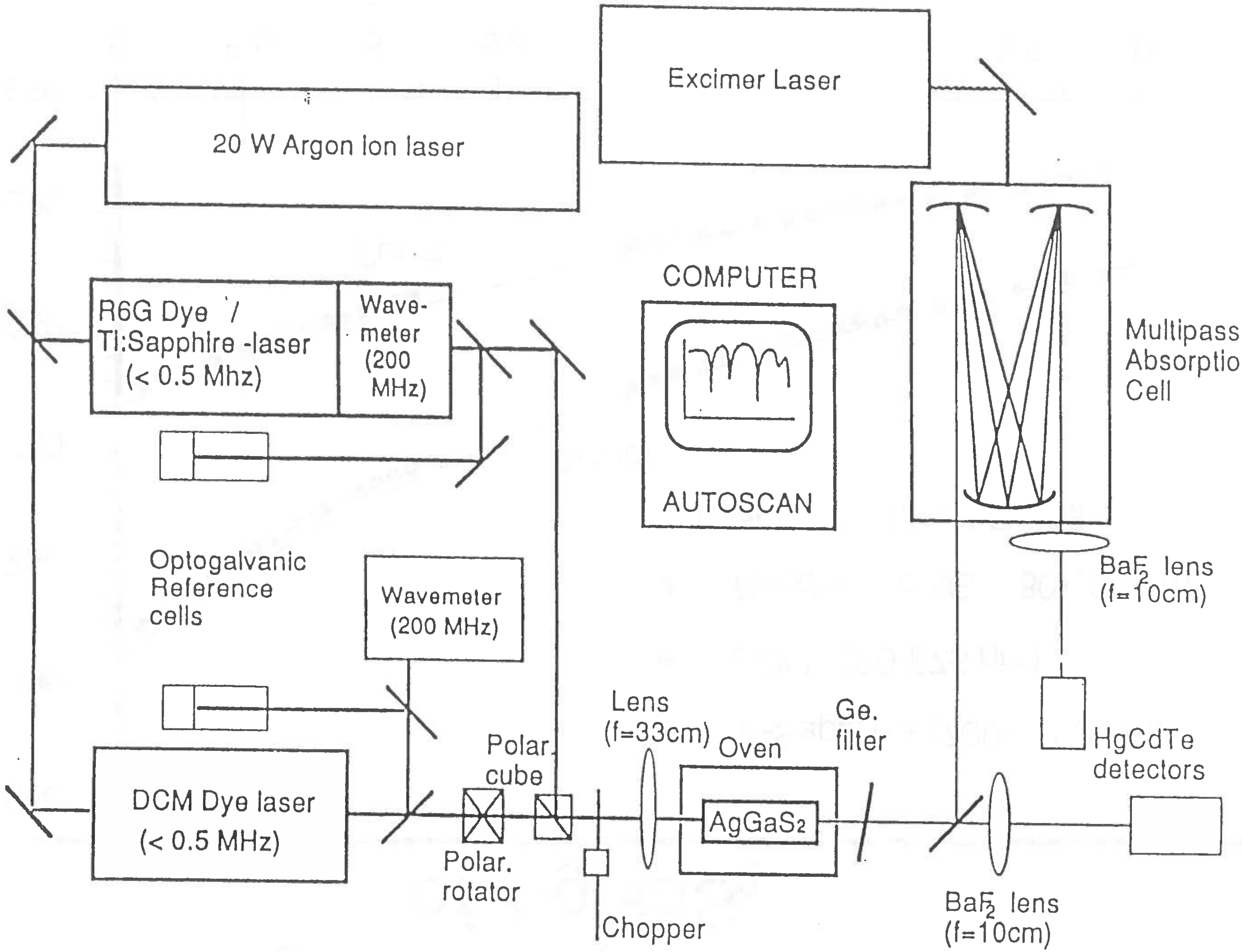
Tuning Characteristics of $AgGaS_2$

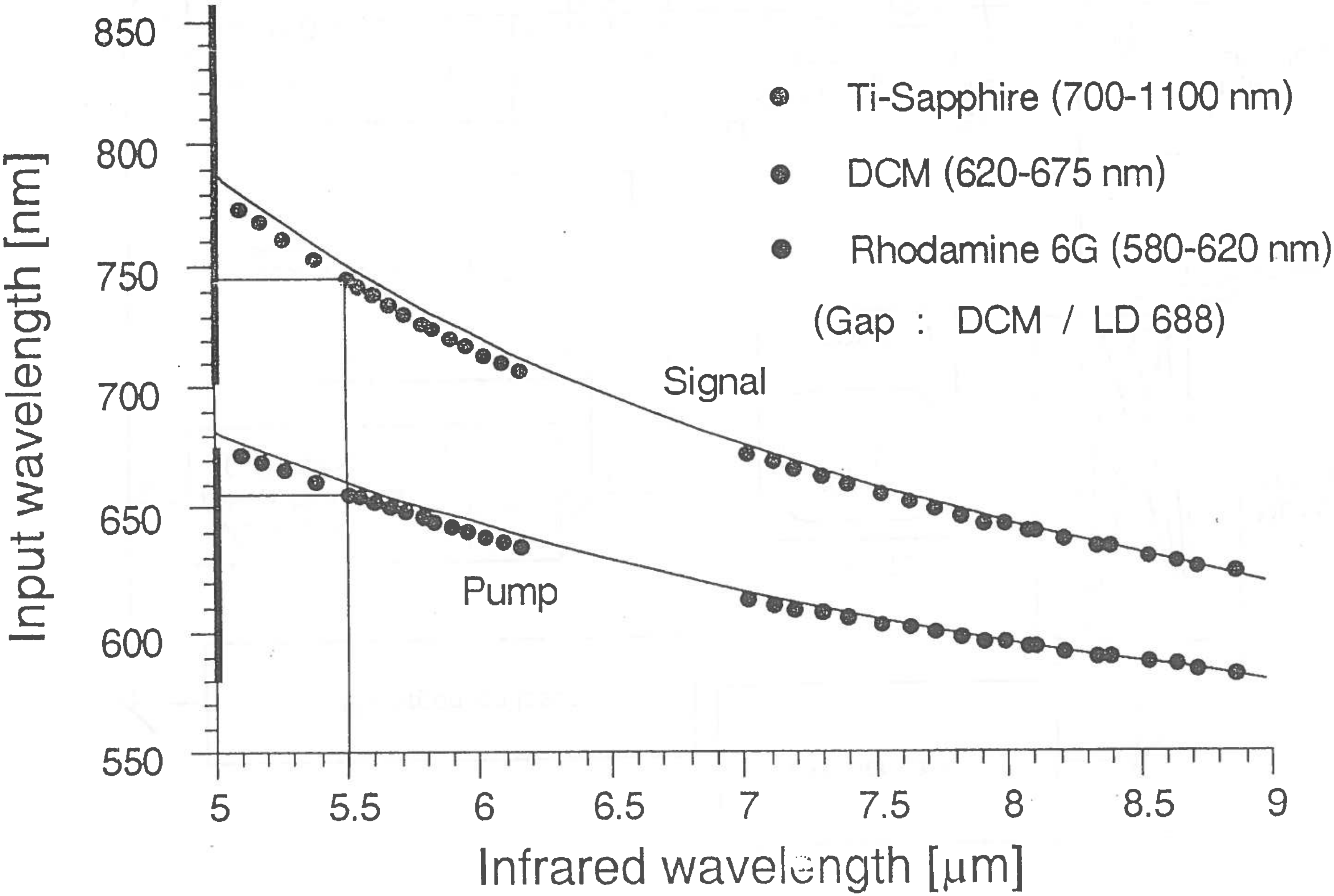


Spectral Characteristics of a Tunable Infrared Laser Based DFG Source

Wavelength Coverage	~ 4 to 9 μm
Resolution	< 1 MHz
Absolute Accuracy	< 200 MHz
Continuously Tunable	~ 1 cm^{-1} (~ 30 GHz)
IR Power	~ > 10 μW (cw)
Divergence	< 5 mrad
Nonlinear Material	$AgGaS_2$
Pump Sources	CW dye, Ti:sapphire, and diode lasers


Excimer Laser
20 W Argon Ion laser
R6G Dye / Ti:Sapphire -laser (< 0.5 Mhz)
Wave-meter (200 MHz)
COMPUTER
AUTOSCAN
Multipass Absorption Cell
Optogalvanic Reference cells
Wavemeter (200 MHz)
BaF2 lens (f=10cm)
Lens (f=33cm)
Ge. filter
Oven
AgGaS2
Polar. cube
HgCdTe detectors
DCM Dye laser (< 0.5 MHz)
Polar. rotator
Chopper
BaF2 lens (f=10cm)

Wavelength Tuning Characteristics of $AgGaS_2$



Barbeq

RQI Molecular Spectroscopy Group

R.F. Curl: Spectroscopy

- Propargyl Radical, $H_2C\text{-}C \equiv CH$
- HCCN
- CO Stretch of Ketenyl, 2040 cm^{-1}

G.P. Glass & R.F. Curl: Chemical Kinetics

- Propargyl Recombination
- Thermal de NO_x Branching Ratios
- HCCO Reaction Rates
- NH_2 + O Kinetics

F.K. Tittel & R.F. Curl: Laser Development & Nonlinear Optics

- IR Difference Frequency Generation

Recent Spectroscopic Accomplishments

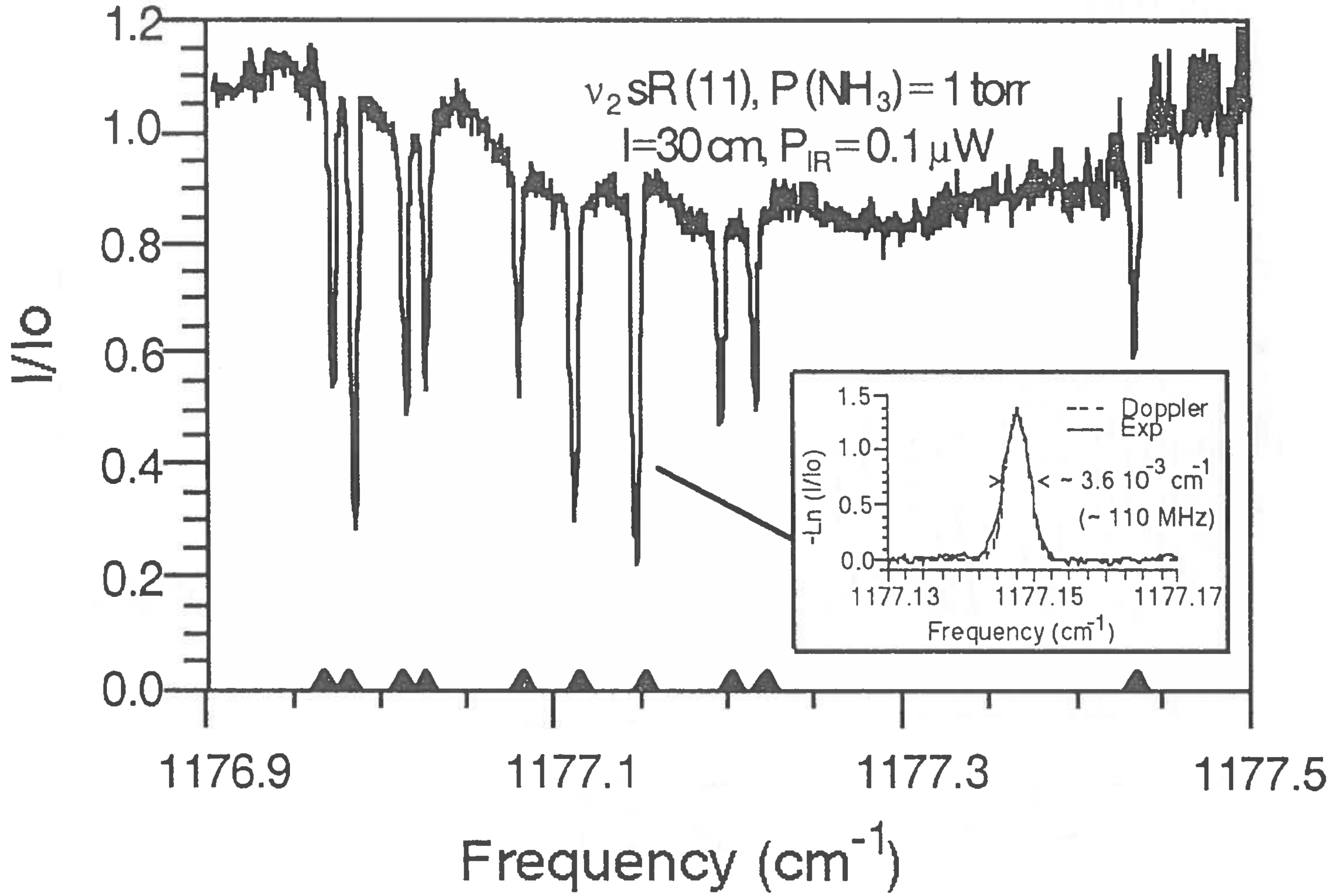
∗ Absorption Spectroscopy

- ν_2 band NH_3 @ 1195 cm^{-1}
- $\nu_1 + \nu_2$ band N_2O @ 1880 cm^{-1}

∗ Infrared Kinetic Spectroscopy (IRKS)
$RX + h\nu \rightarrow R. + X.$

- CO vibr. excited states near 2100 cm^{-1}
- HOCO ν_2 band Q-branch near 1852 cm^{-1}
- DOCO ν_2 band Q-branch near 1850 cm^{-1}
- HCCN ν_2 CCN asymmetric stationary motion near 1745 cm^{-1}

High Resolution Absorption Spectrum of NH_3 near 1177 cm^{-1}



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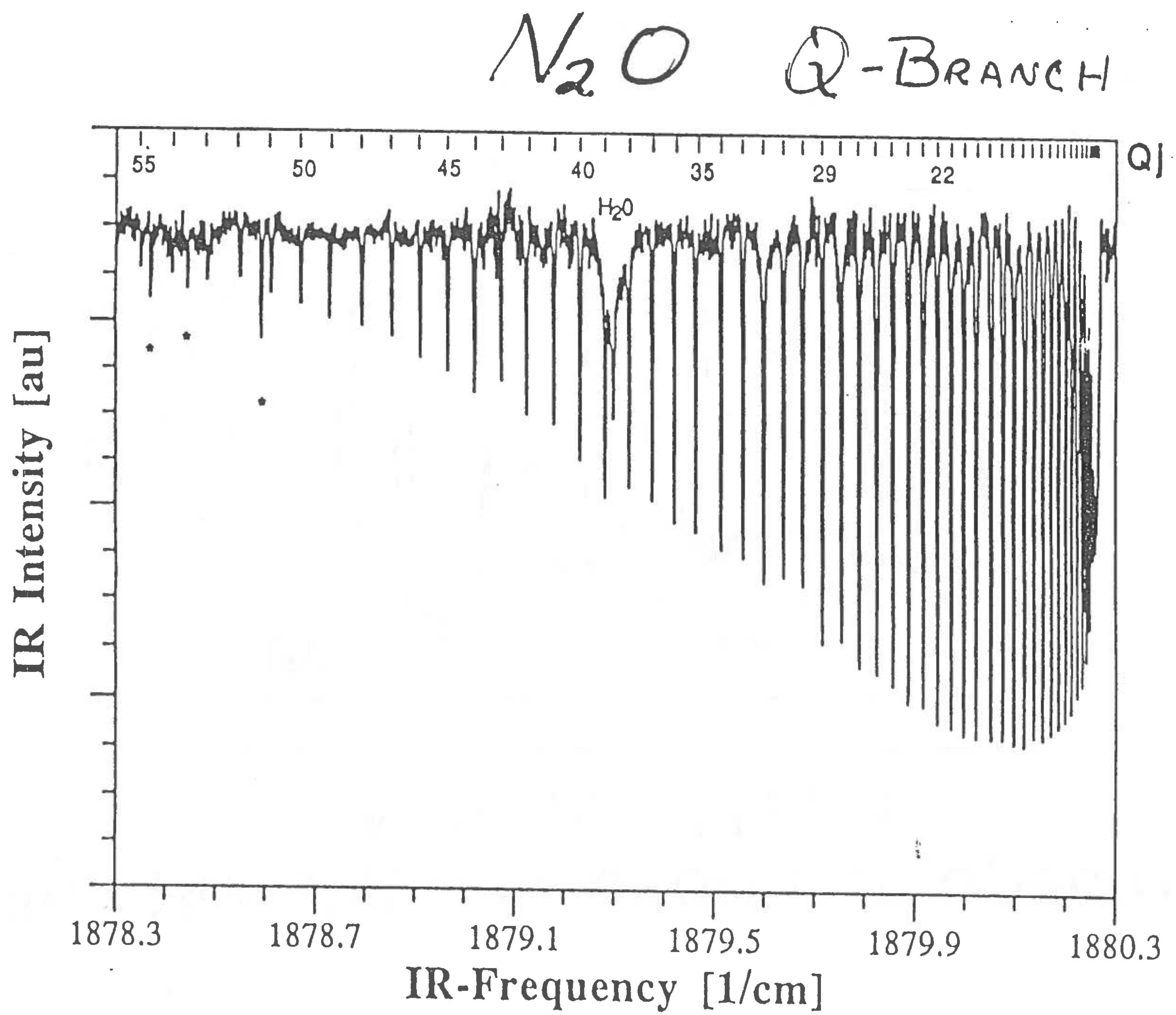
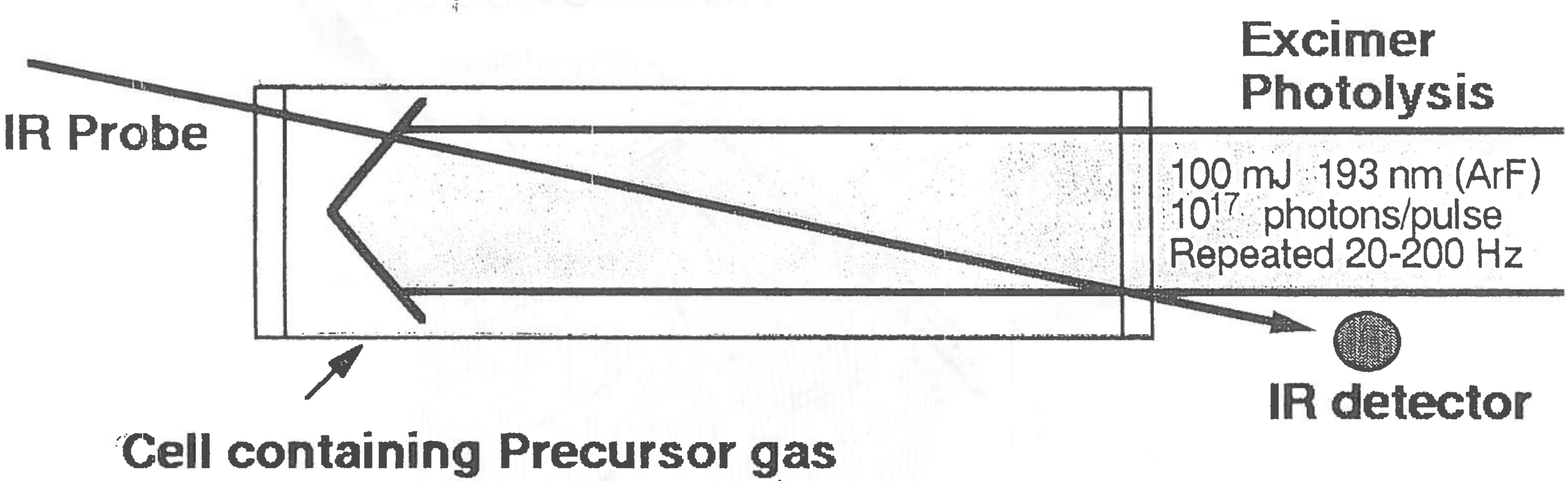


N2O Q-BRANCH
QJ
55
50
45
40
35
29
22
H2O
IR Intensity [au]
1878.3
1878.7
1879.1
1879.5
1879.9
1880.3
IR-Frequency [1/cm]

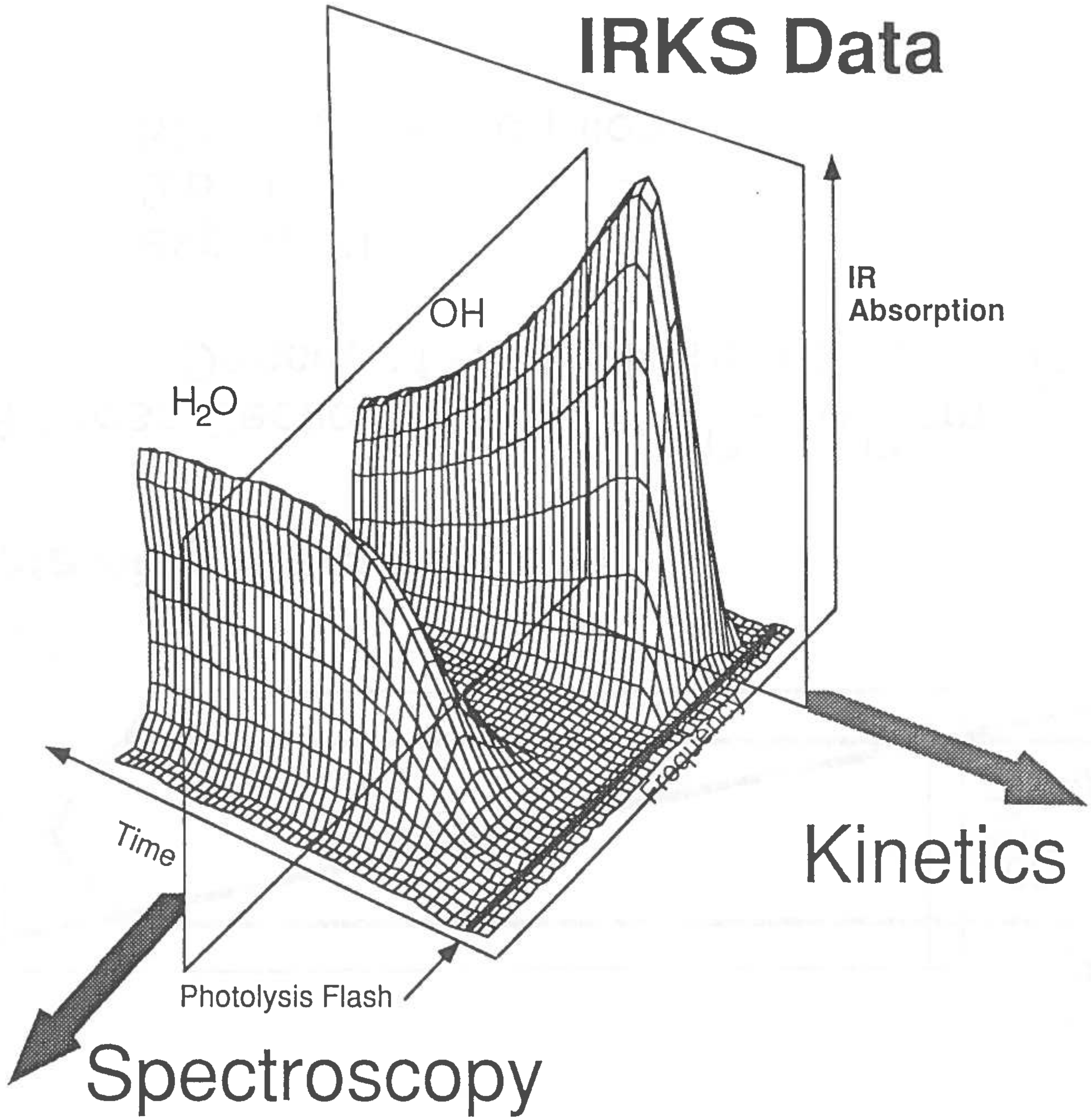
Infrared Kinetic Spectroscopy Apparatus



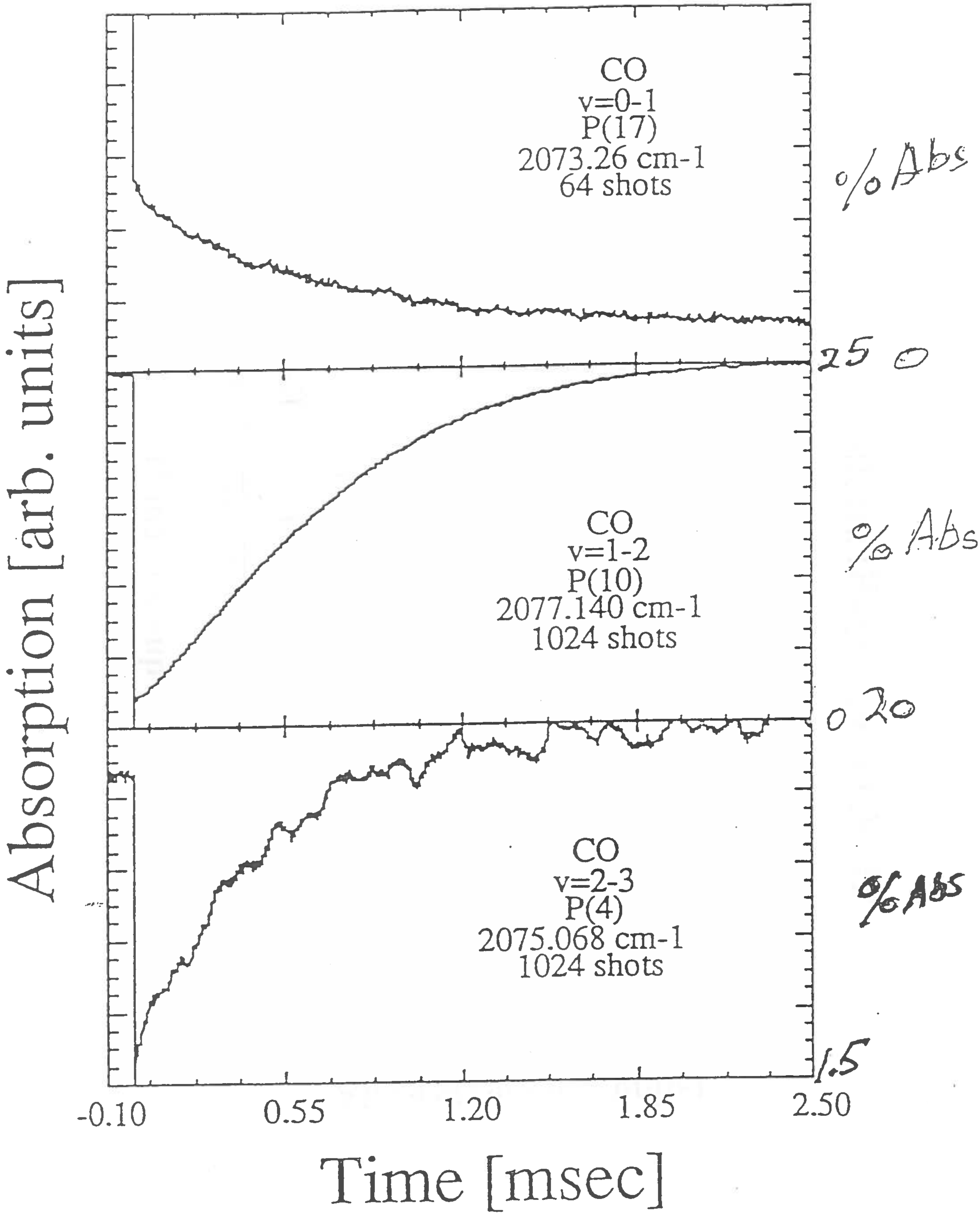
σ_o = IR Cross-Section (Peak) ~ 10^{-17} - 10^{-19} cm^2
NL = Column Density of Radical Absorbers ~ $10^{17}/cm^2$

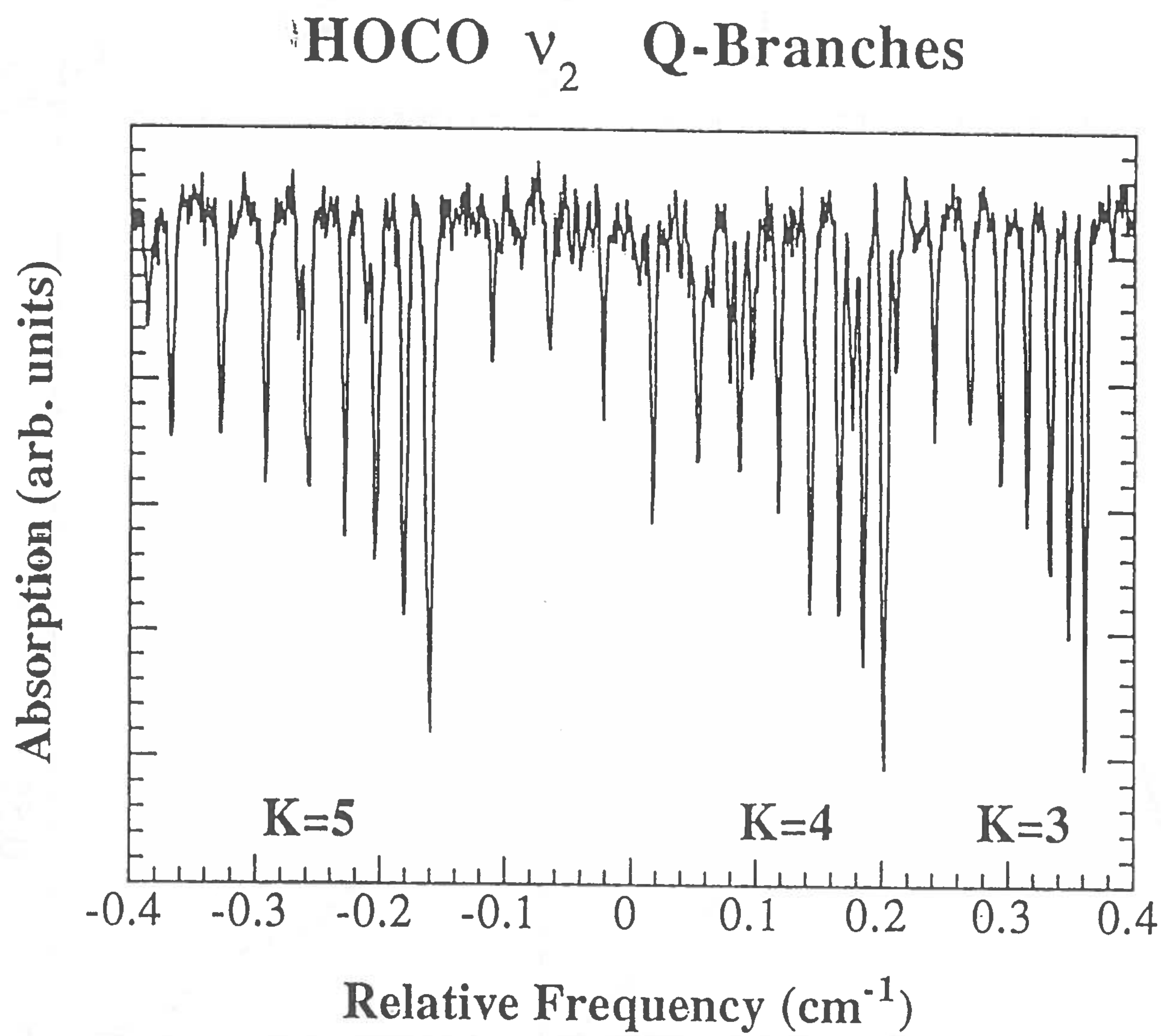
$(\Delta P/P)_{IR}$ = $\exp(-\sigma_o NL)$
~ 0.6 - 0.01
~ 60% - 1% Absorption

IRKS Data

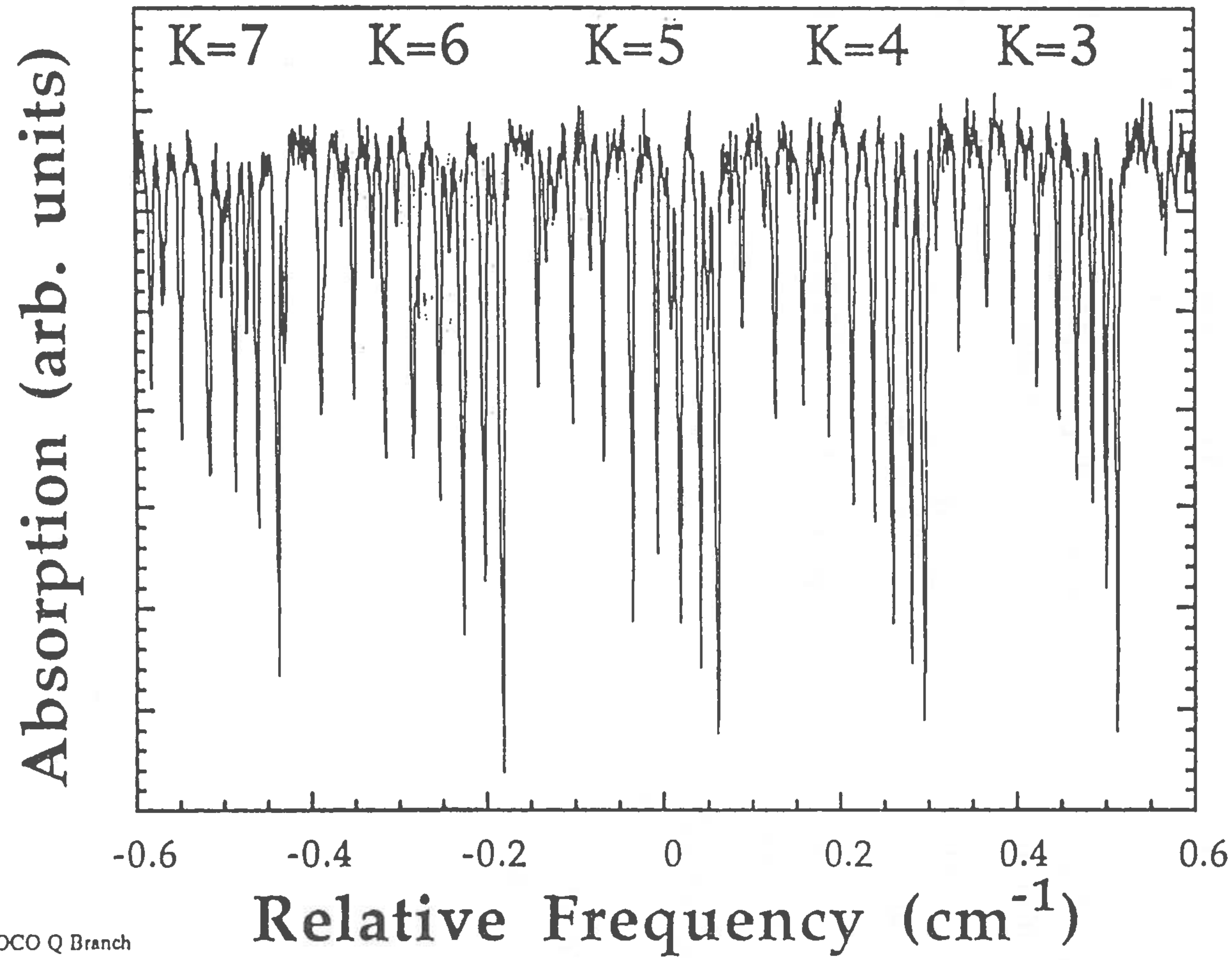


IR
Absorption
OH
H_2O
Time
Frequency
Photolysis Flash
Kinetics
Spectroscopy

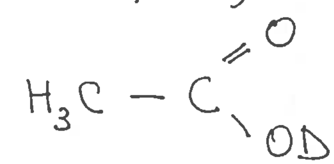

CO
v=0-1
P(17)
2073.26 cm-1
64 shots
CO
v=1-2
P(10)
2077.140 cm-1
1024 shots
CO
v=2-3
P(4)
2075.068 cm-1
1024 shots
Absorption [arb. units]
-0.10
0.55
1.20
1.85
2.50
Time [msec]
%Abs
25
0
%Abs
0
20
%Abs
1.5


HOCO ν2 Q-Branches
Absorption (arb. units)
K=5
K=4
K=3
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
Relative Frequency (cm-1)

DOCO ν_2 Q-Branch



Photolysis, 193nm



Center frequency: 1850 cm^{-1}

Los Alamos 16/DOCO Q Branch

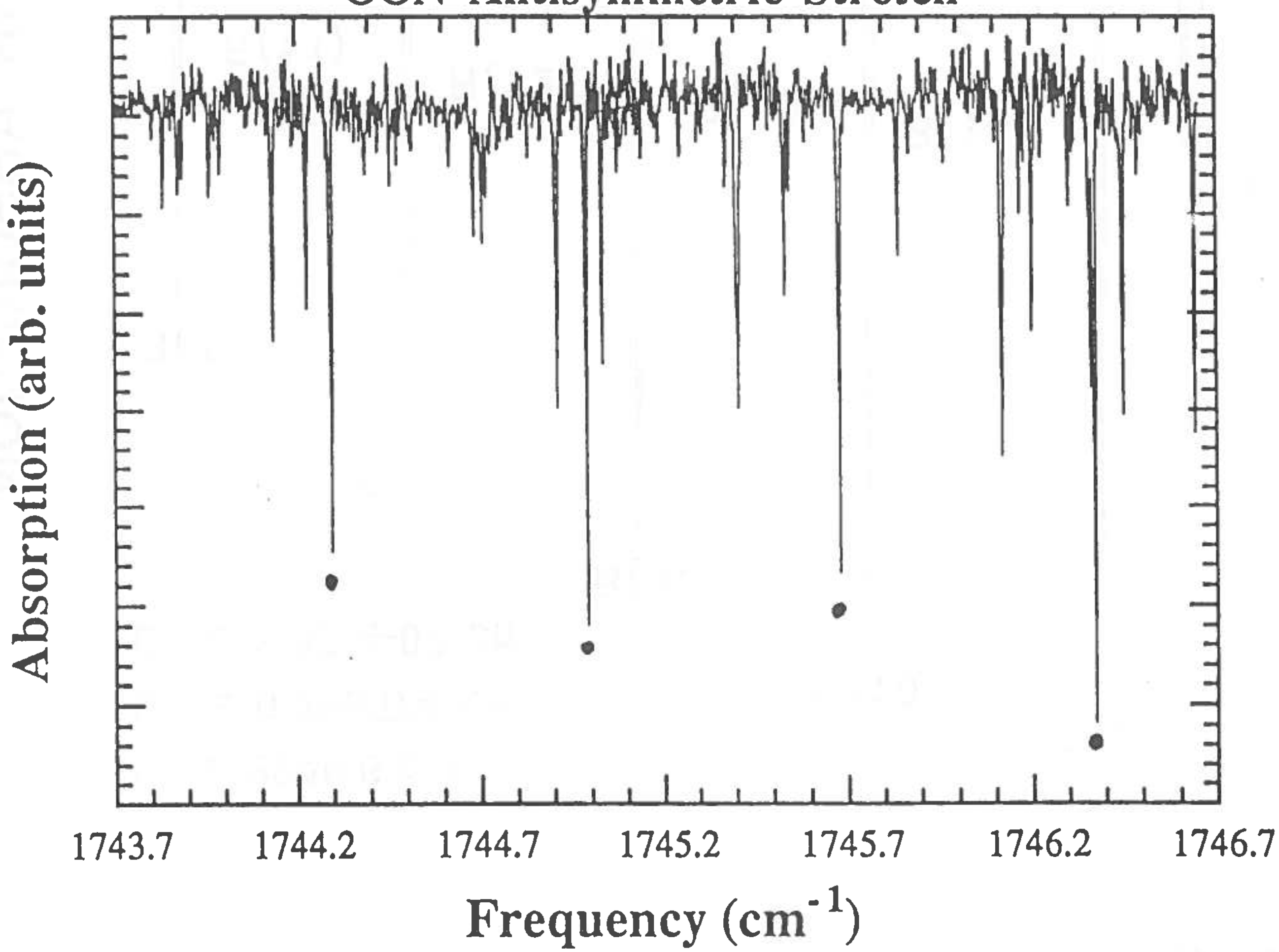
HCCN Equilibrium Geometry

Linear	Bent	Quasi-Linear
EPR (1964,1965) Bernheim et al.	Ab Initio (1979) Zandler, Schaefer et al.	CCI (1988) Roos et al.
EPR (1970) Bernheim et al.	Ab Initio (1983) Kim, Schaefer et al.	MW (1990) Brown, Saito, Yamamoto
Huckel (1968) Hoffmann et al.	MR-CISD (1987) Rice , Schaefer	IRKS (1993) Farhat, Morter, Curl
EPR (1970) Wassermann et al.	CCSD(T) (1992) Seidl, Schaefer	MW (1993) Saito, Endo
Matrix IR (1977) Dendramis and Leroi	QCISD(T) (1993) Aoki et al.	IRKS (1993) Miller, Eckhoff, Curl
Ab Initio (1978) Dendramis and Leroi		
MW (1984) Saito, Endo, Hirota		

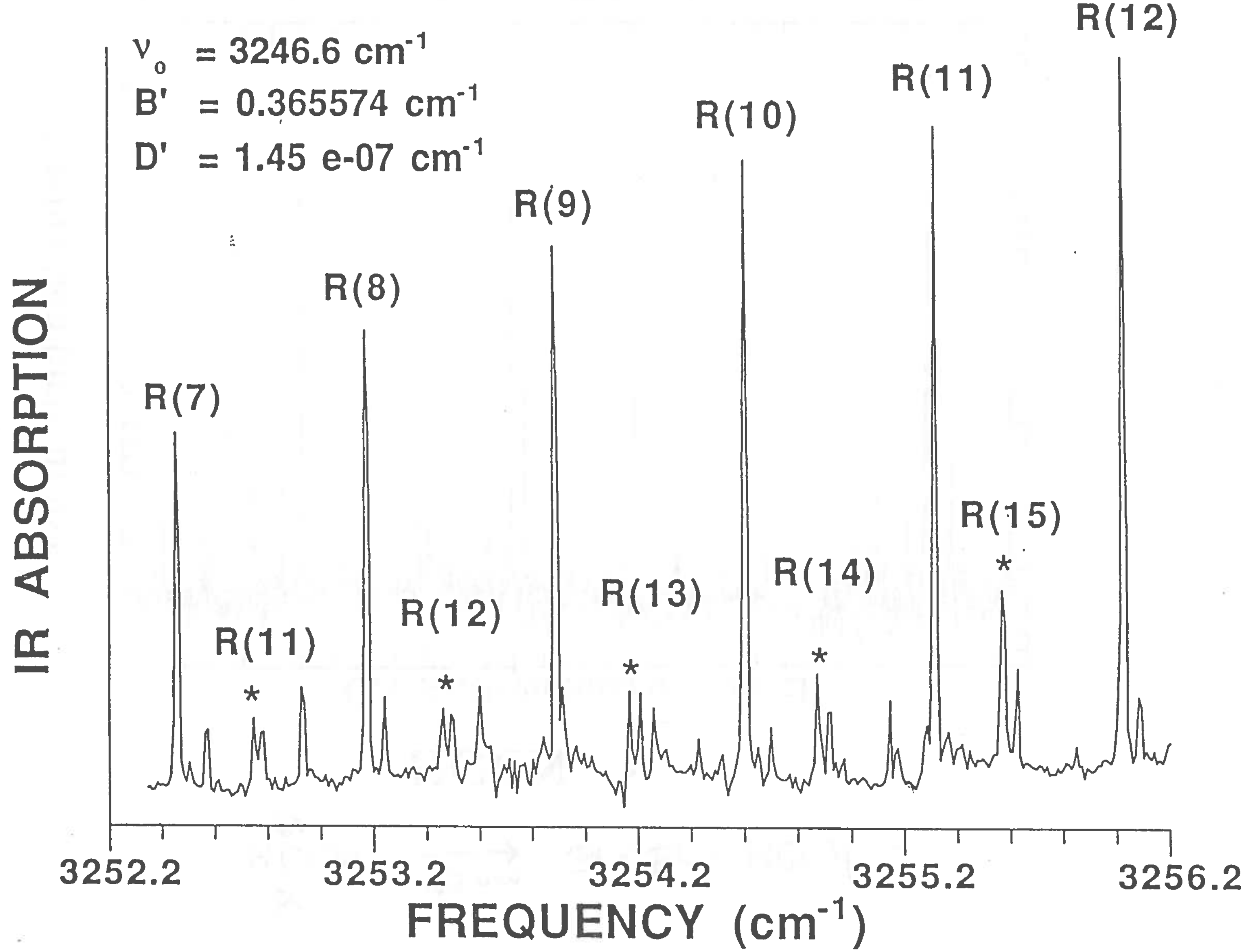
$$HCBr_2CN \xrightarrow{193\ nm} Br + Br + \underline{HCCN}$$

HCCN ν_2

CCN Antisymmetric Stretch

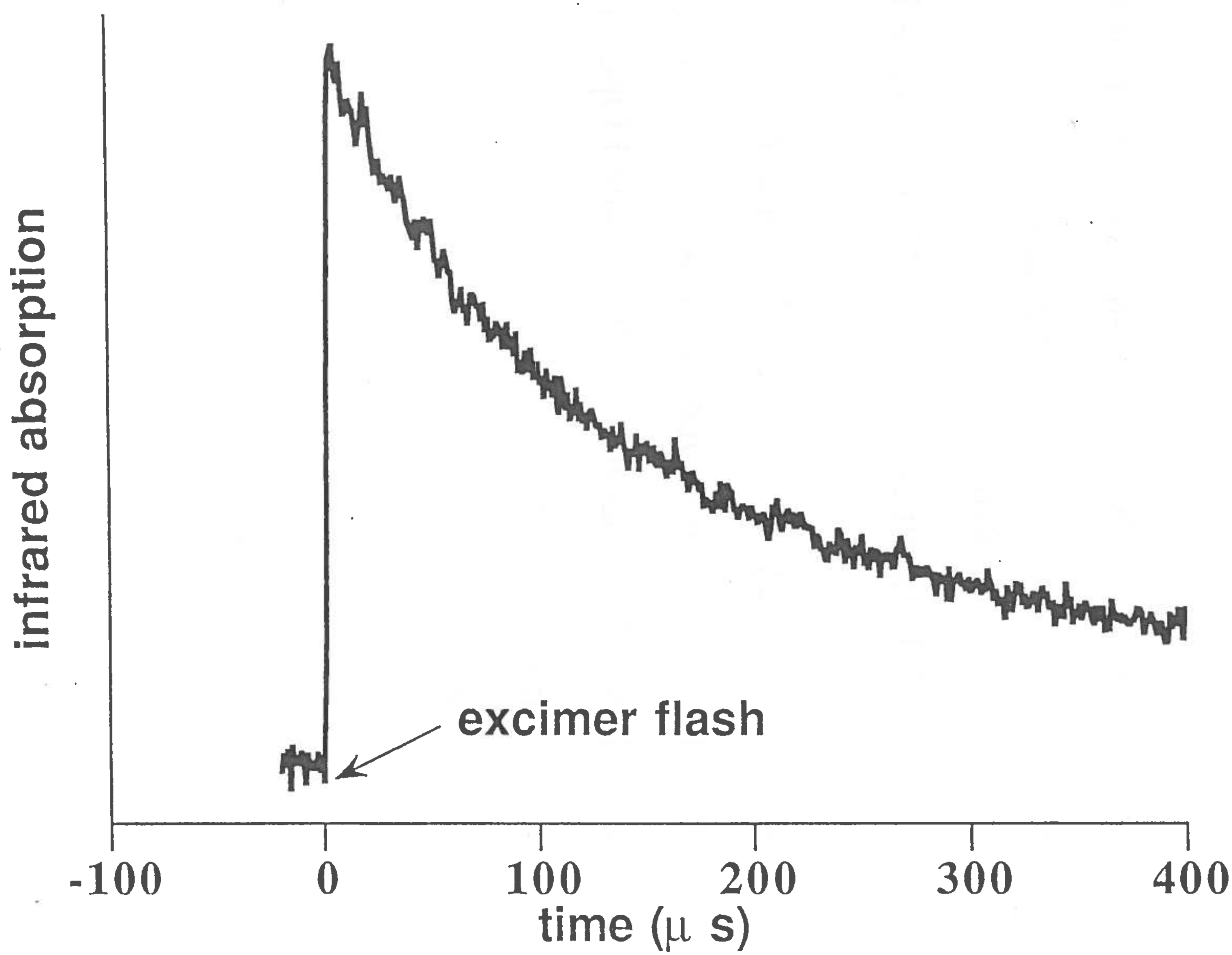


C.L.Morter, S.K.Farhat, R.F.Curl, *Chem. Phys. Lett.* 203, 153 (1993)



HCCN Decay Profile

$Br_2HCCN + h\nu(193\ nm) \longrightarrow Br + Br + HCCN$



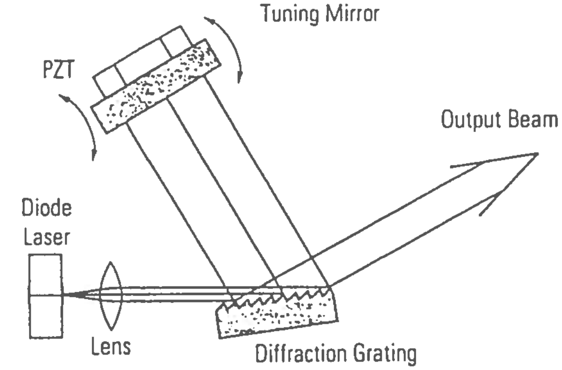
Advantages of Diode Laser Pumping

* Scalable to High Peak and Average Power
* Broad Wavelength Coverage
  (~ 0.6 to 3 μm)
* High Efficiency Source of Narrow Band Radiation
  (η_{elec} ~ 40%)
* Frequency and Amplitude Control
* Long Lifetime Operation > 20,000 hours
* Room Temperature or TE Cooled Operation
* Compact Size
* Cost

Continuous Tuning Without Mode-Hopping

Tunable External Cavity Diode Laser:

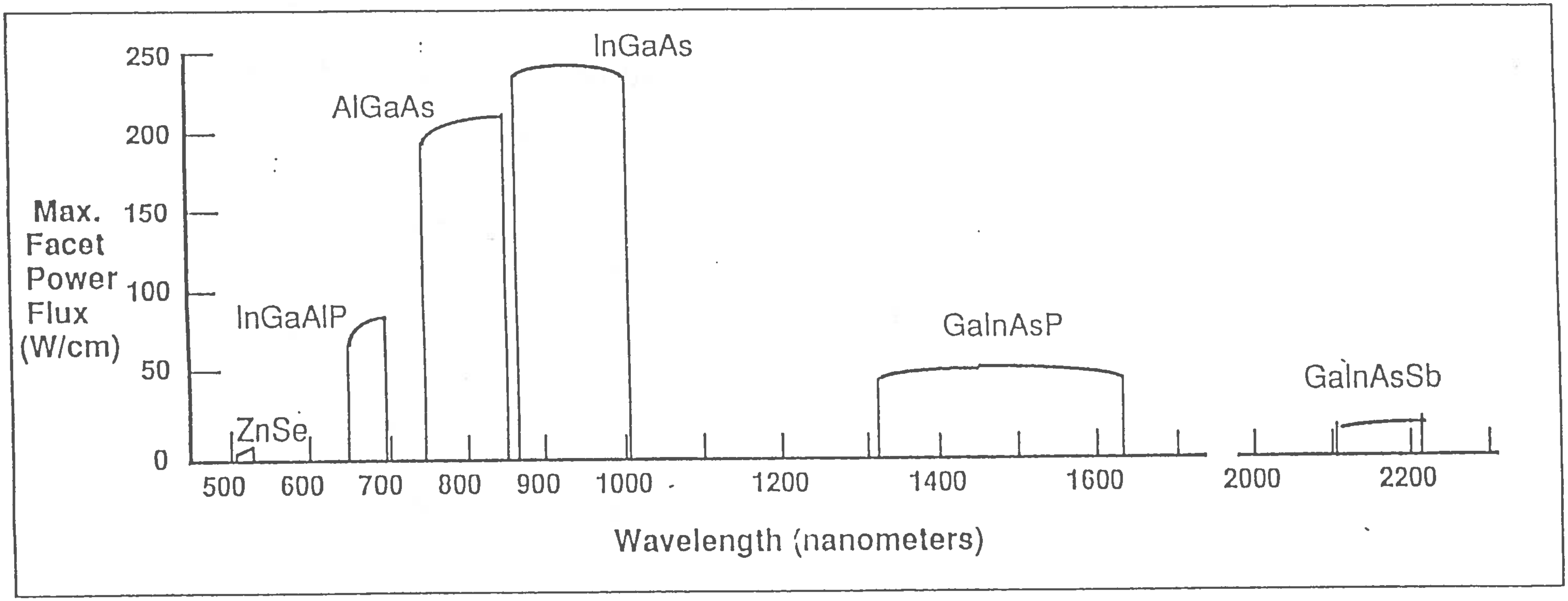
* 100-kHz linewidth.
* Continuous tuning over a 12-nm range from a compact module. 60-GHz tuning without mode-hopping.
* 0.01 nm/day stability. 10-MHz stability over a period of one minute.
* Amplitude modulation up to 10 MHz.



A grating used in the Littman grazing-incidence configuration is used as the frequency-selective component in the external cavity laser.

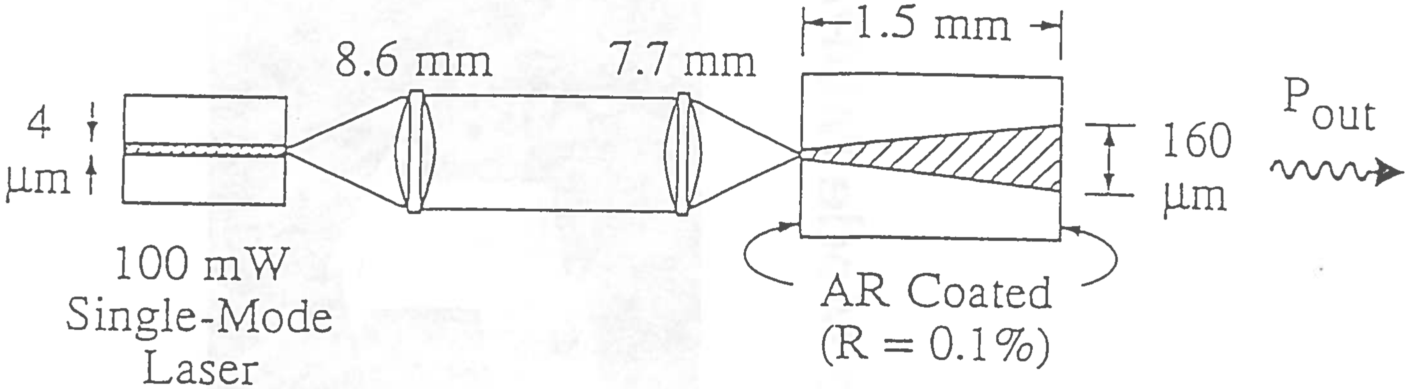
ν Focus Model 6102

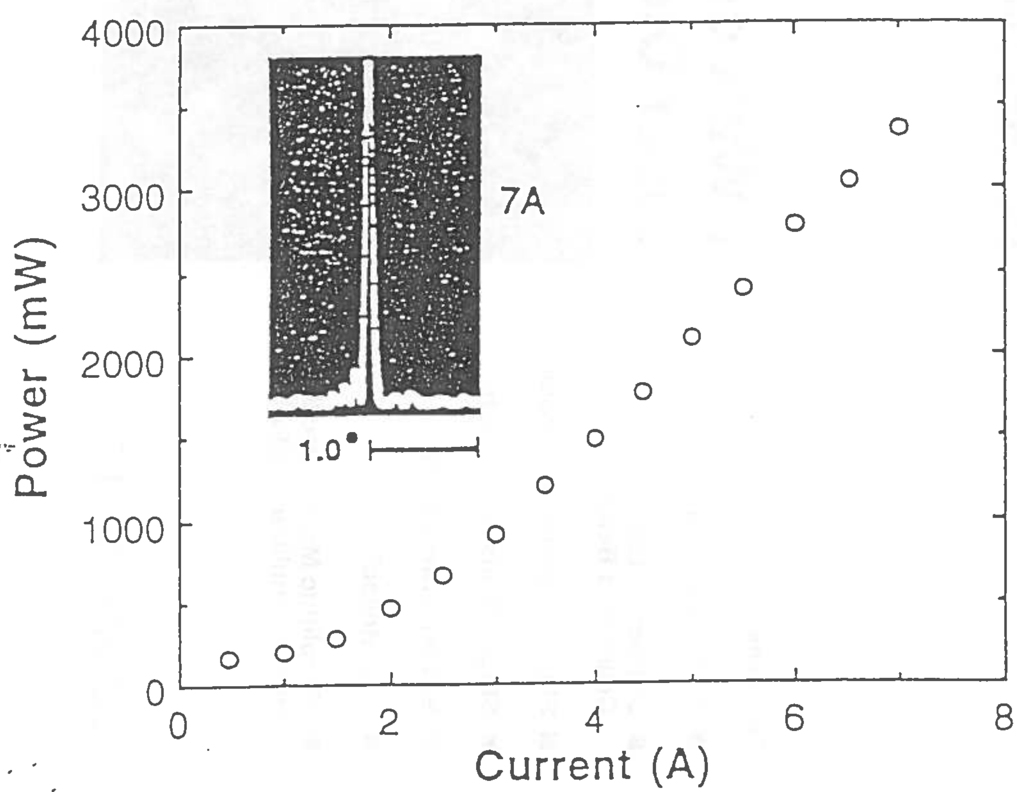
Representative Diode Performance
(Quasi-CW, Room Temperature)



Source: W.F. Krupke, LLNL, 1992

Discrete Flared Amplifier MOPA

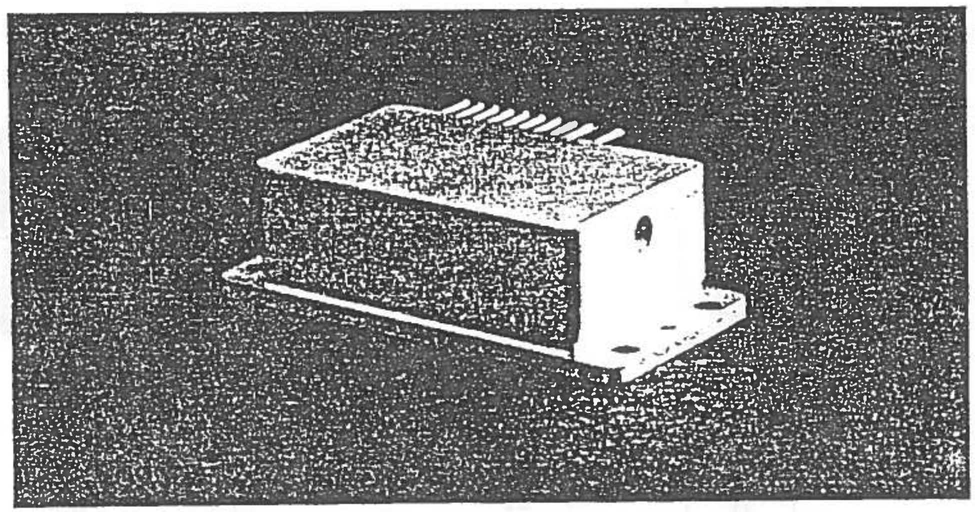




Light-current curve for cw operation, Pi=400 mW

Spectra Diode Labs

1 Watt cw Single Mode MOPA Laser Diode

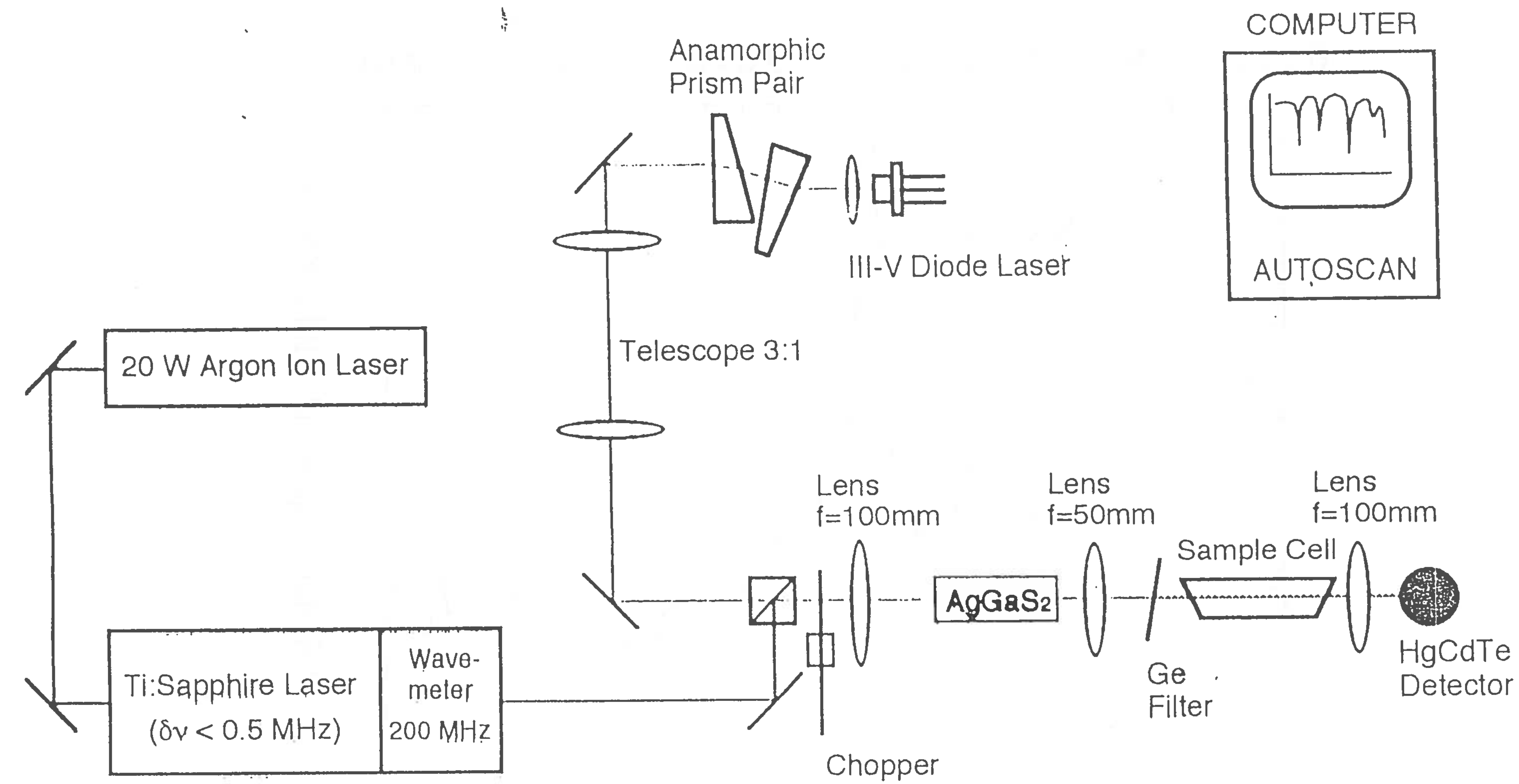


Features

- 1 Watt cw Power
- Diffraction Limited, Collimated Beam
- Single Longitudinal Mode
- Single Transverse Mode
- 985 nm Wavelength
- High Reliability
- Monolithic Master Oscillator/ Power Amplifier (MOPA)

SDL™-5760 SERIES

Diode/Ti:Sapphire Mixing Experiment



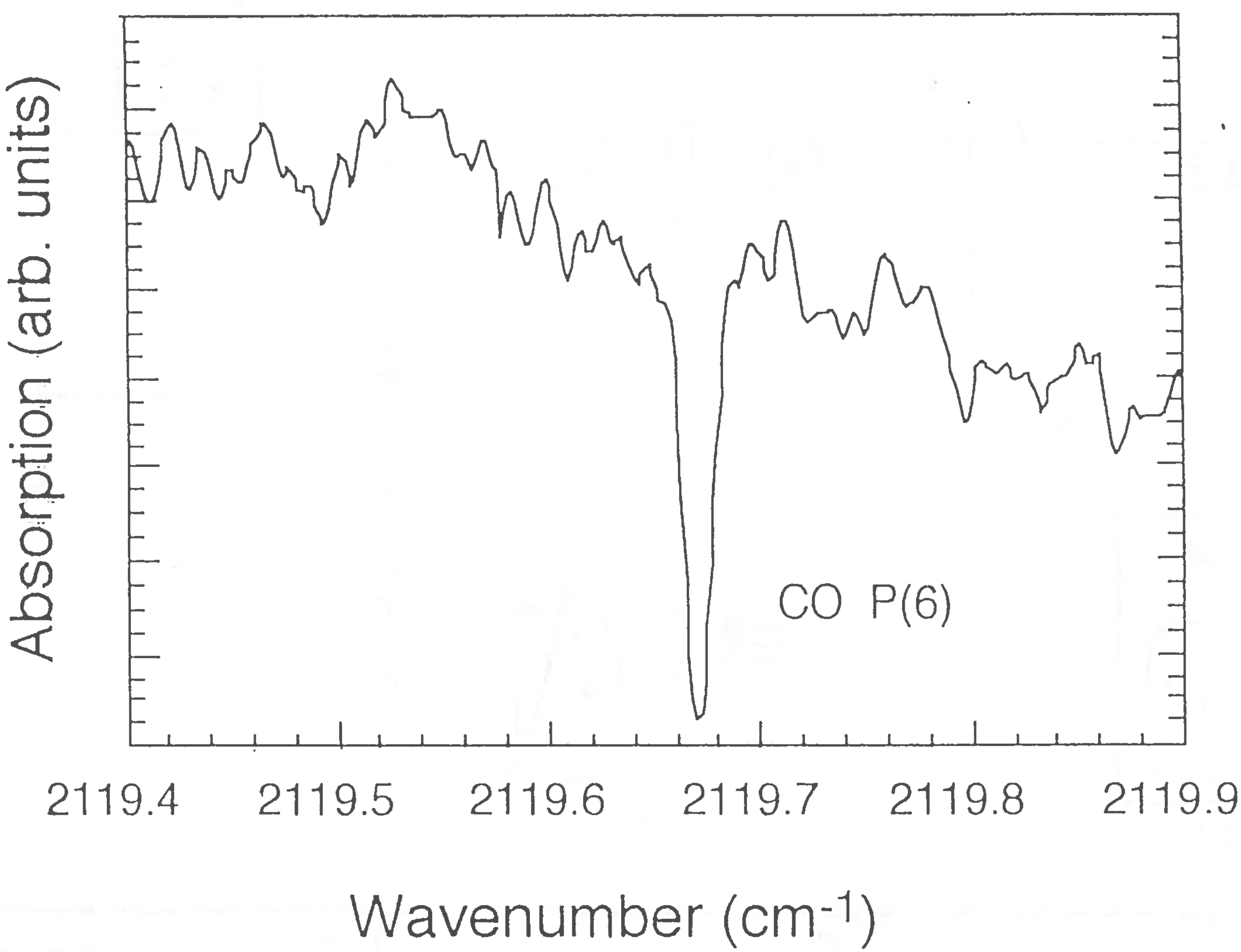
<u>Ti:Sapphire laser</u>
$\lambda = 808.3$ nm
$P_{max} = 1W$

<u>Toshiba TOLD 9140(s)</u>
$\lambda = 690.3$ nm
$P = 12.1$ mW

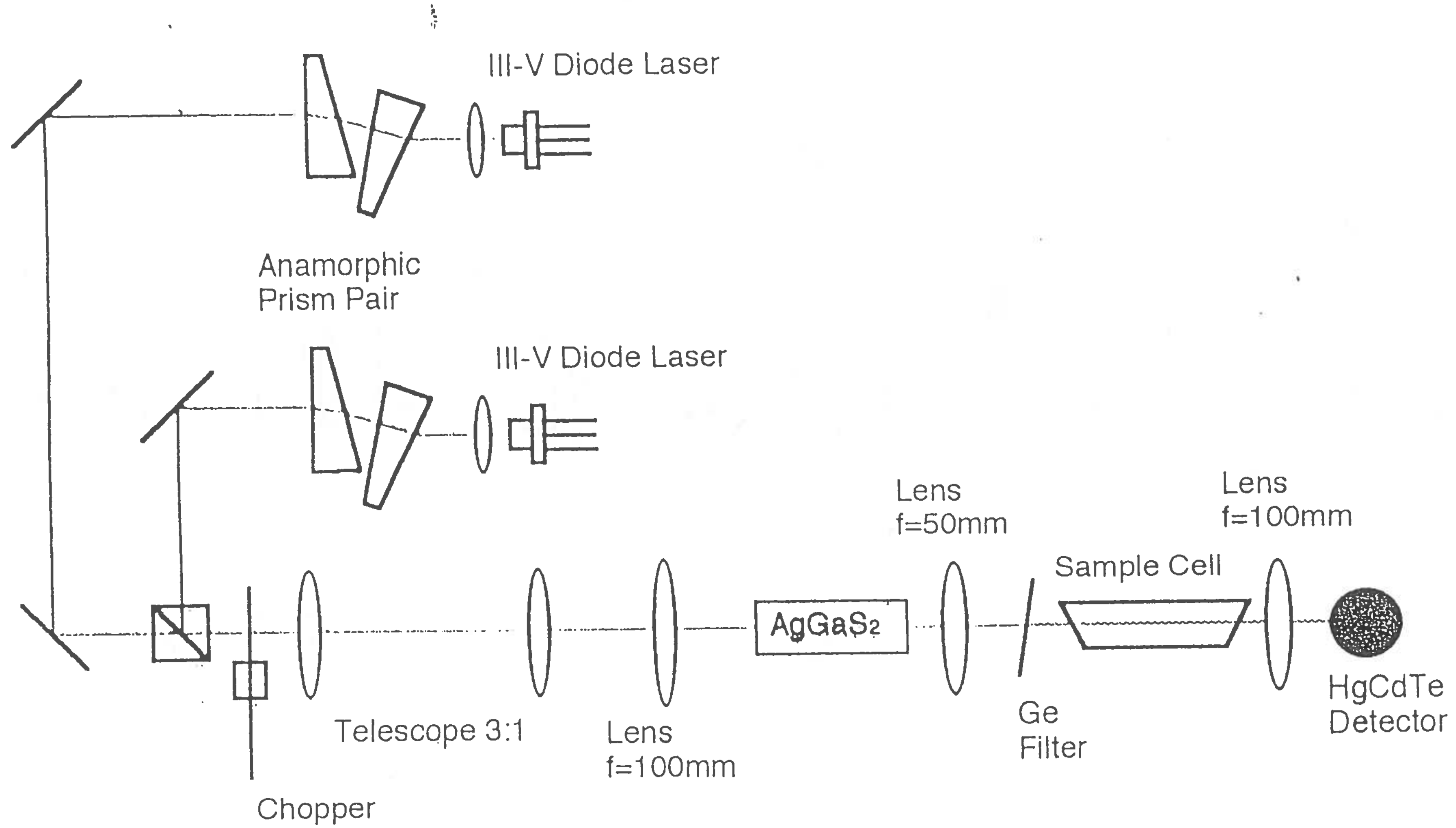
<u>DFG output</u>
$\lambda = 4.73\ \mu m$
$P_{max} = 1.4\ \mu W$

Cooperation with R.G. Hulet group

CO Absorption Spectrum Detected with the Diode/Ti:Sapphire Pump Laser Configuration



Diode/Diode Mixing Experiment



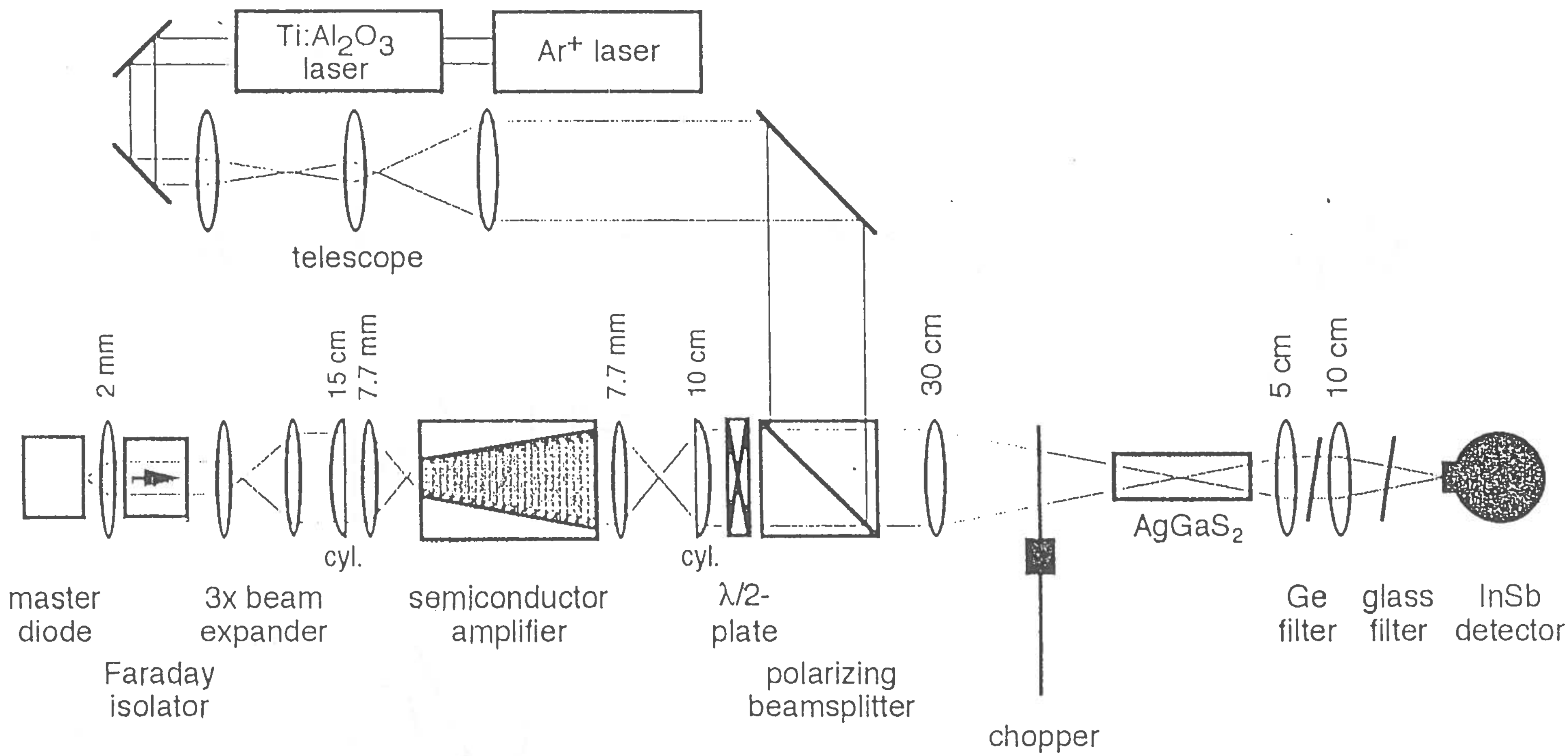
<u>Sharp LT010MD</u>
$\lambda = 808$ nm
P = 1.93 mW

<u>Toshiba TOLD 9140(s)</u>
$\lambda = 690$ nm
P = 10.1 mW

<u>DFG output</u>
$\lambda = 4.73$ µm
P = 3.3 nW

Cooperation with
R.G. Hulet group

Tapered Amplifier/Ti:Sapphire Mixing Experiment



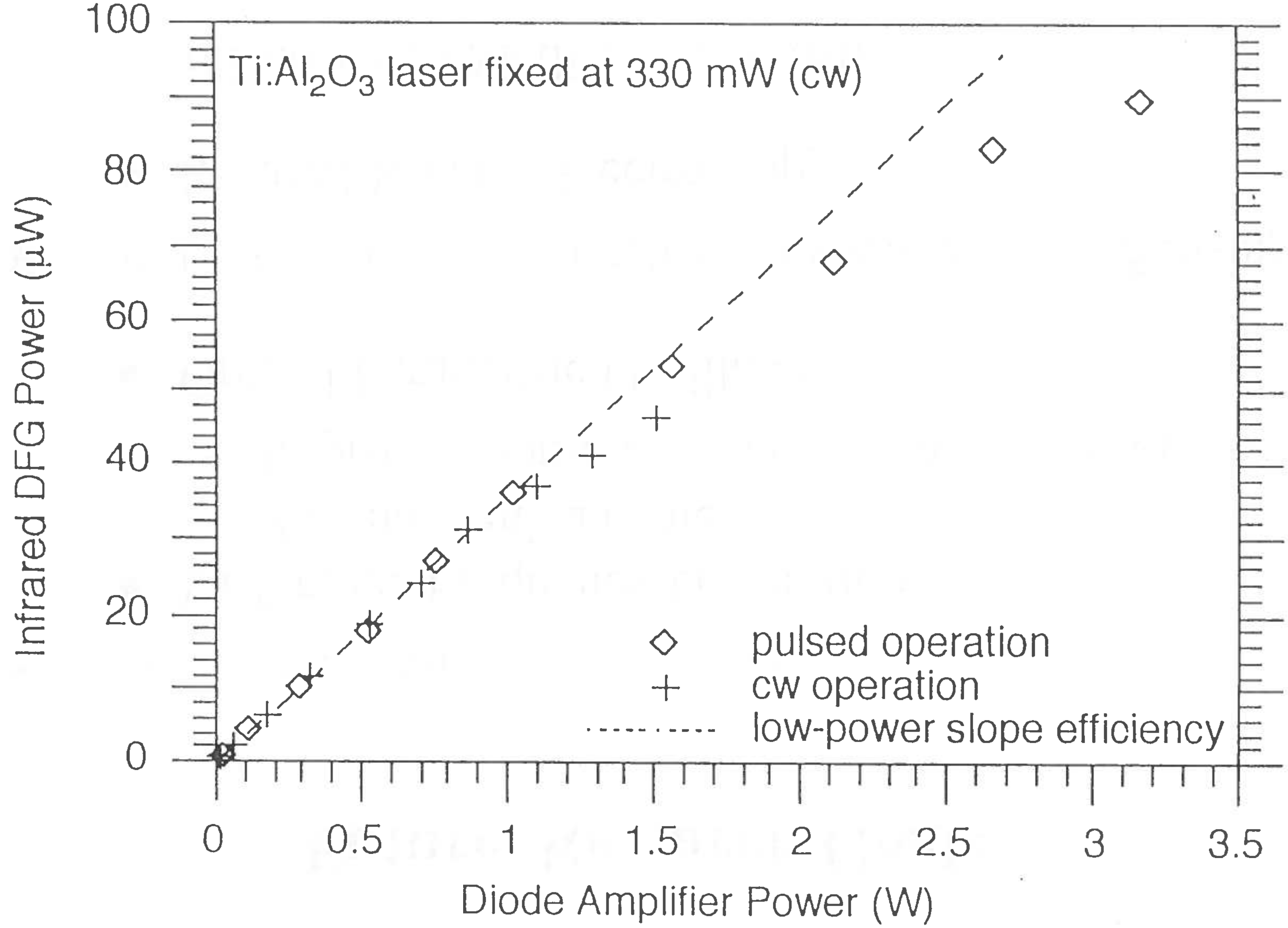
<u>Master Diode SDL5410C</u>
λ = 858.6 nm
P = 130 mW

<u>Tapered Amplifier</u>
λ = 860 nm
P_{max} = 2.5 W

<u>Ti:Sapphire Laser</u>
λ = 714.6 nm
P = 330 mW

Cooperation with
L. Goldberg
Naval Research Lab

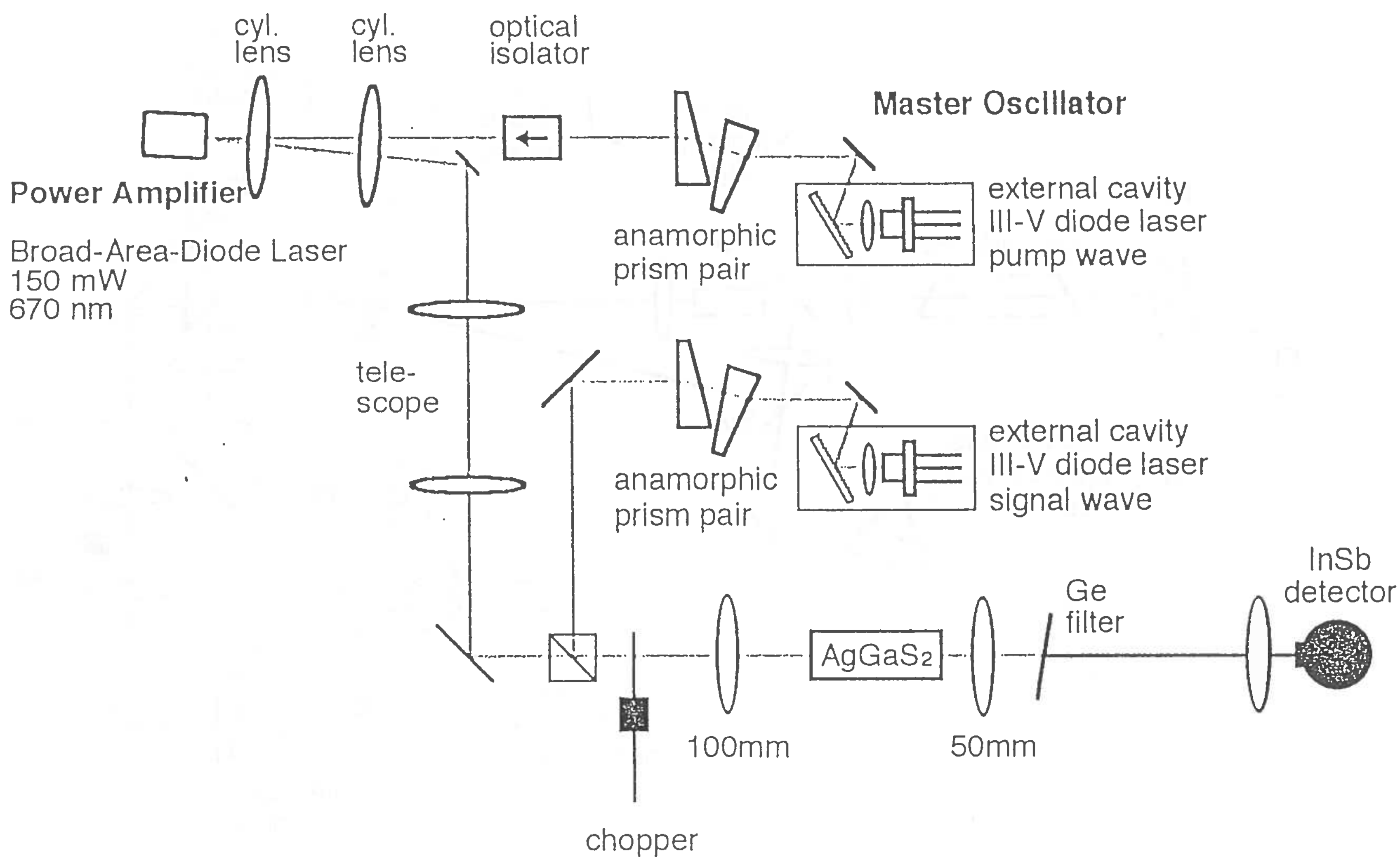
Tapered Amplifier/Ti:Sapphire Laser



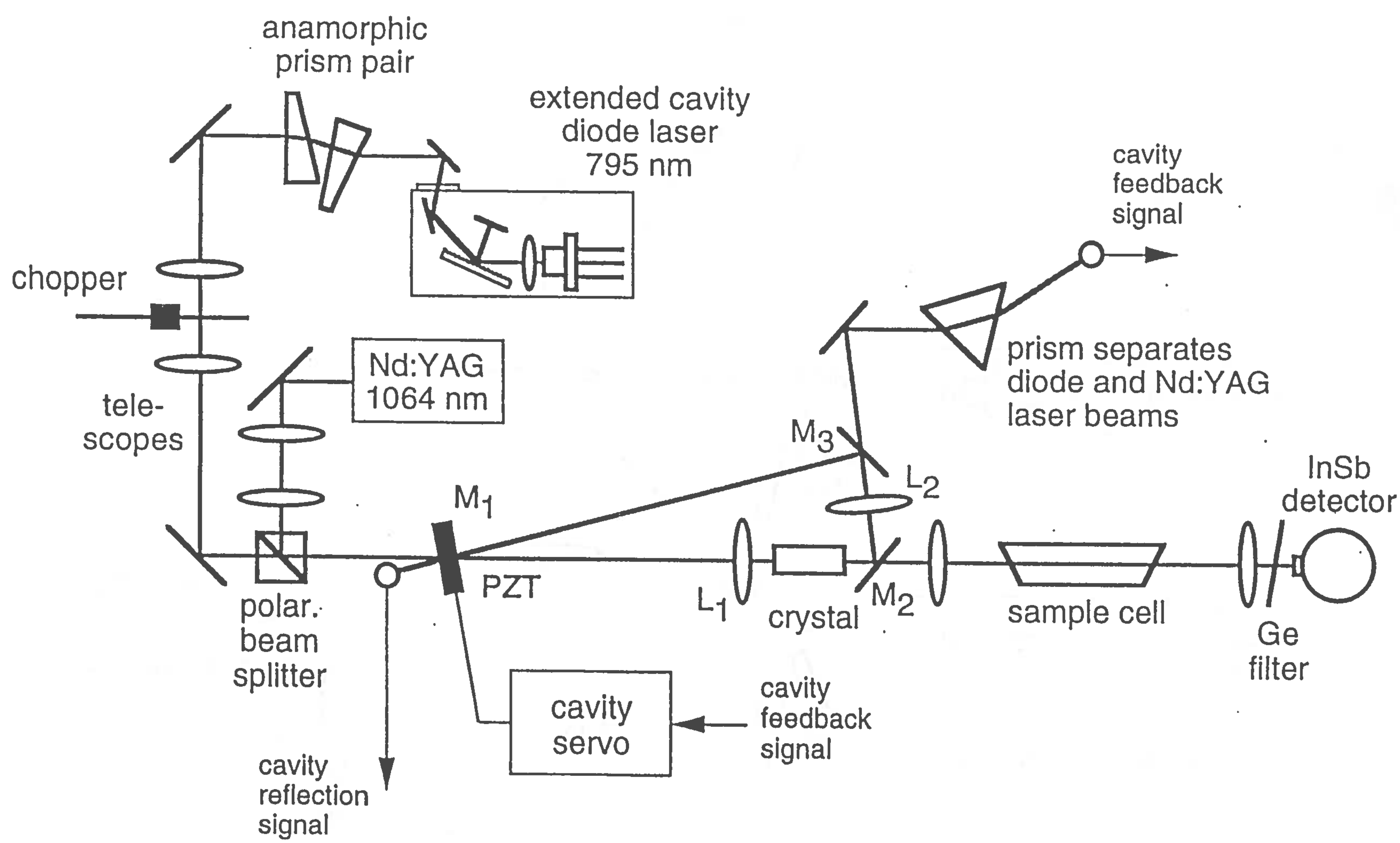
Future Research Goals

* Nonlinear Frequency Extension
    - Difference Frequency Generation
        - Resonant enhancement
        - Improved nonlinear materials & pump sources
    - Optical Parametric Oscillators
* Extension to Laser Spectroscopy and Remote Sensing
    - Infrared Kinetic Spectroscopy
* Applications in Medical Diagnostics

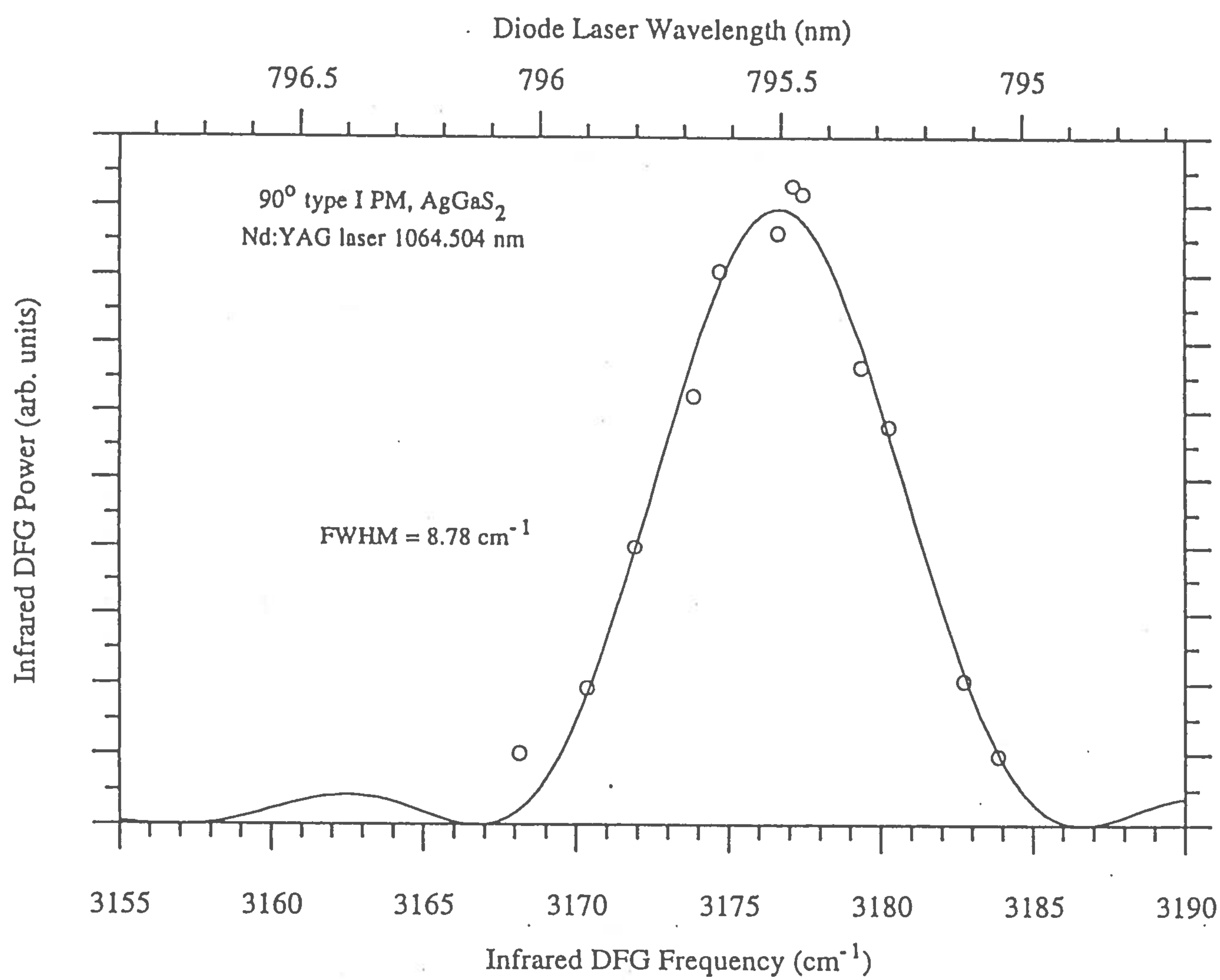
DFG Using Optical Semiconductor Amplifier



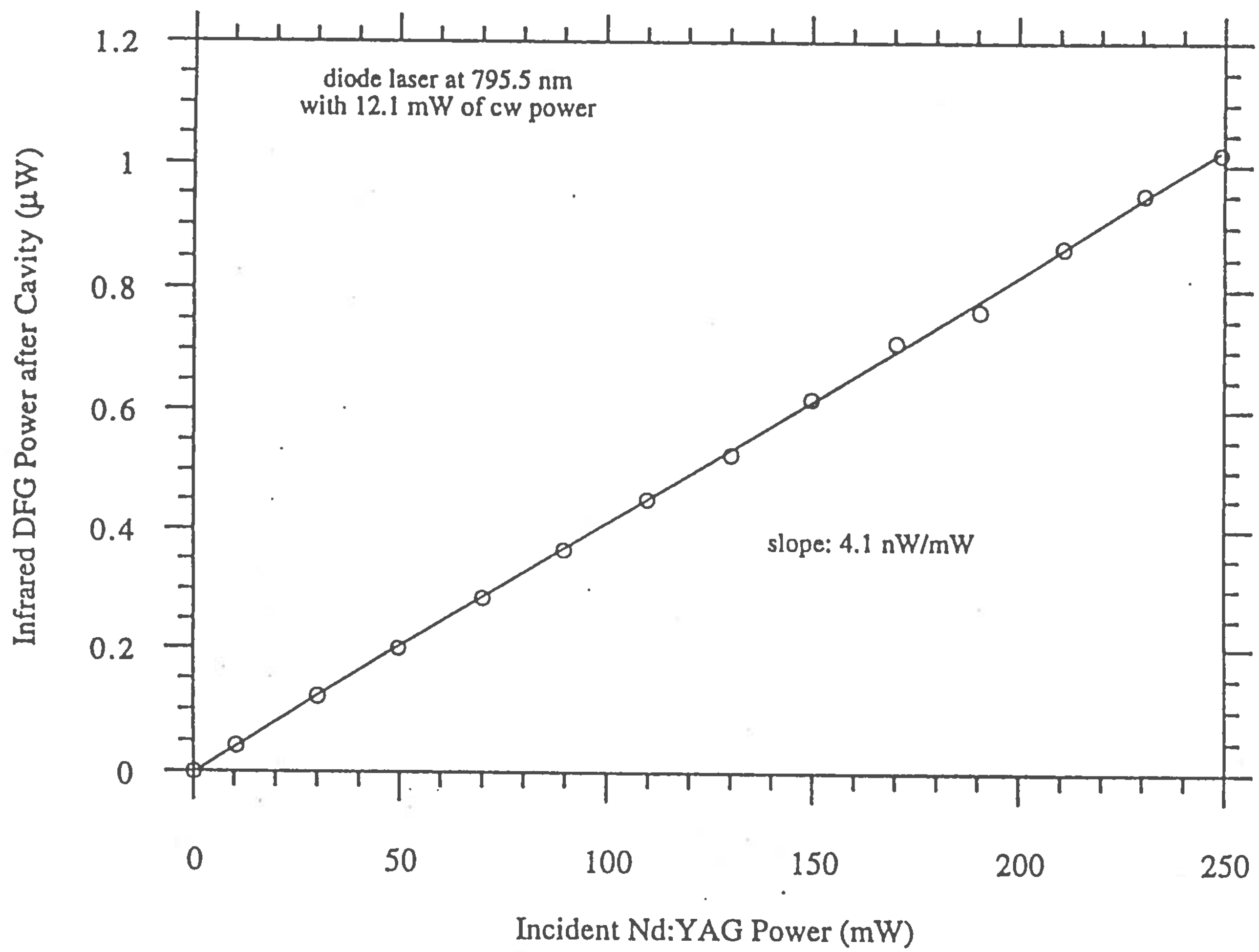
EXPERIMENTAL SETUP FOR AN EXTERNAL CAVITY DIFFERENCE-FREQUENCY SOURCE



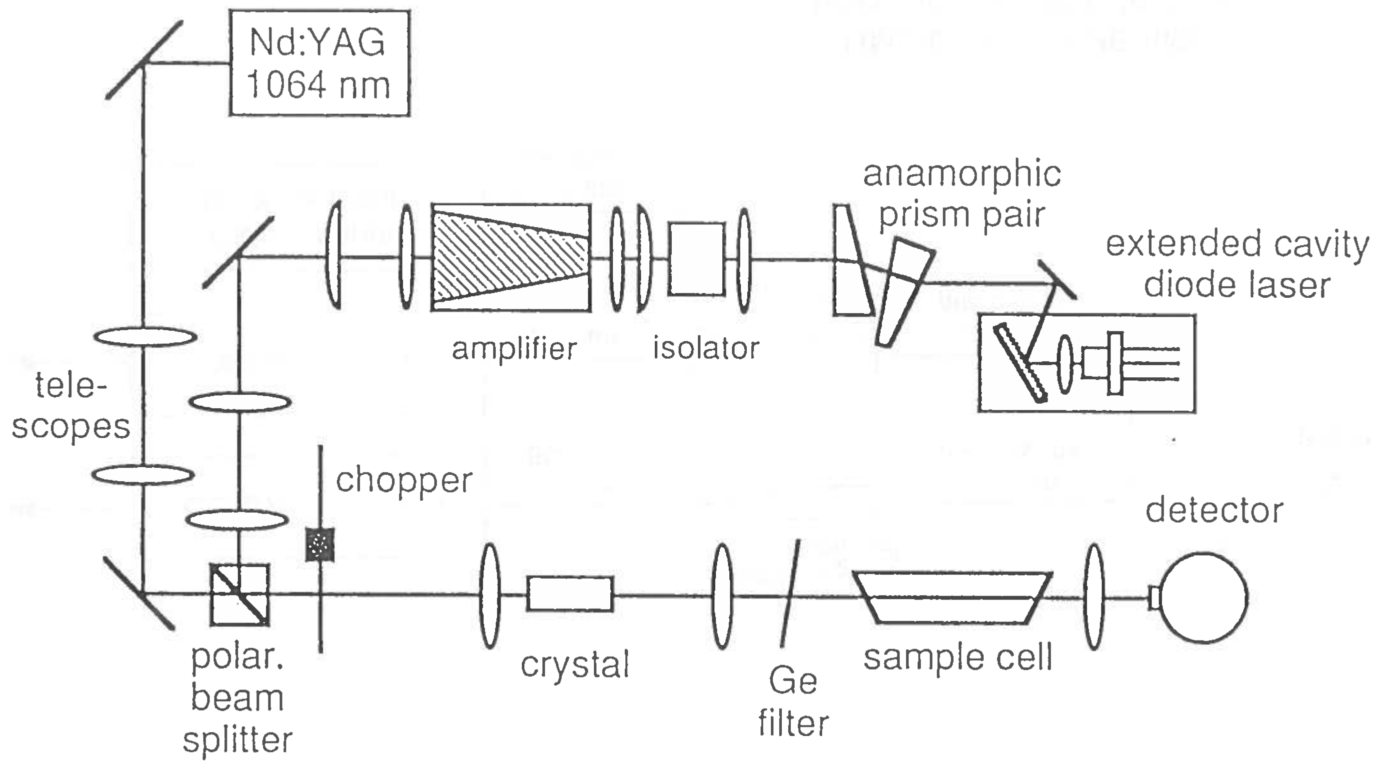
PHASEMATCHING BANDWDTH OF THE DFG MIXING PROCESS

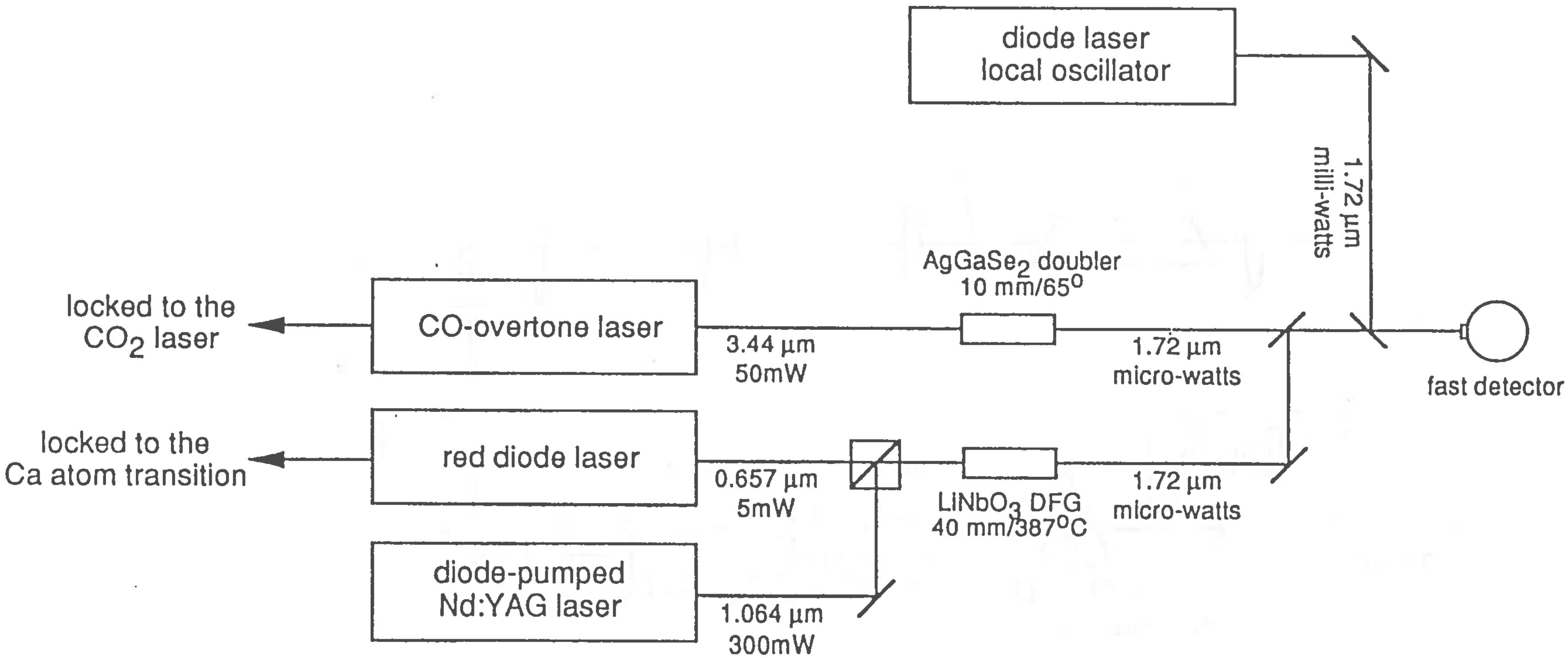


GENERATED INFRARED DFG POWER AS A FUNCTION OF Nd:YAG LASER PUMP OUTPUT



All Solid State Infrared DFG Sensor





TIME-CHAIN-EXPERIMENT
using DFG and SFG techniques

Summary

∗ DFG Spectrometer Using Dye/Ti:Sapphire Lasers
- Tuning Range: 4 to 9 μm
- Single-Frequency Scan: ~ 1 cm^{-1}
- Spectral Linewidth: $\Delta\nu < 1$ MHz
- IR Power: Several 10 μW (~ 300 μW)

∗ High Resolution Infrared Spectroscopy
- Vibrationally Excited CO
- ν_2 Fundamental Vibration of HOCO ~ 1852.5 cm^{-1}
- ν_2 Fundamental Vibration of HCCN ~ 1740 cm^{-1}

∗ DFG Spectrometer Using Diode Lasers & Amplifiers
- IR Power with Diode/Ti:Sapphire: ~ 2 μW
- IR Power with Diode Amplifier/Ti:Sapphire:
  ~ 50 μW cw, ~ 90 μW pulsed

∗ Novel Applications of Compact Mid-Infrared DFG Sources
- Molecular Spectroscopy
- Remote Sensing and Pollution Monitoring

Acknowledgments

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Richard Smalley	K. Petrov
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Department of Energy	Humboldt Foundation