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Optically-Based Diagnostics for Gas-Phase Laser Development

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Overview

- **Theme: multi-species diagnostics for absolute concentrations are essential for effective development of high-energy gas lasers**
  - Precursor production, loss, optimization
  - Transference from subscale reactors
  - Scaling of gain, power, efficiency

- **Current applications**
  - Electric Oxygen Iodine Laser (EOIL): precursor kinetics and gain dynamics
  - Related systems: COIL, micro-COIL
  - Alkali laser systems: DPAL, XPAL gain, multi-photon effects

- **Outline of presentation:**
  - Brief overview of diagnostics and apparatus
  - Absolute emission spectrometry
    - Near-infrared spectroscopy: $O_2(a^1\Delta_g)$, $I(^2P_{1/2})$
    - Air afterglow photometry: $O(^3P)$
  - Ultrasensitive absorption photometry: I_2, O_3
  - High-resolution absorption/gain spectroscopy: atomic iodine, alkali metals

Role of Optical Diagnostics in High Energy Gas Laser Development

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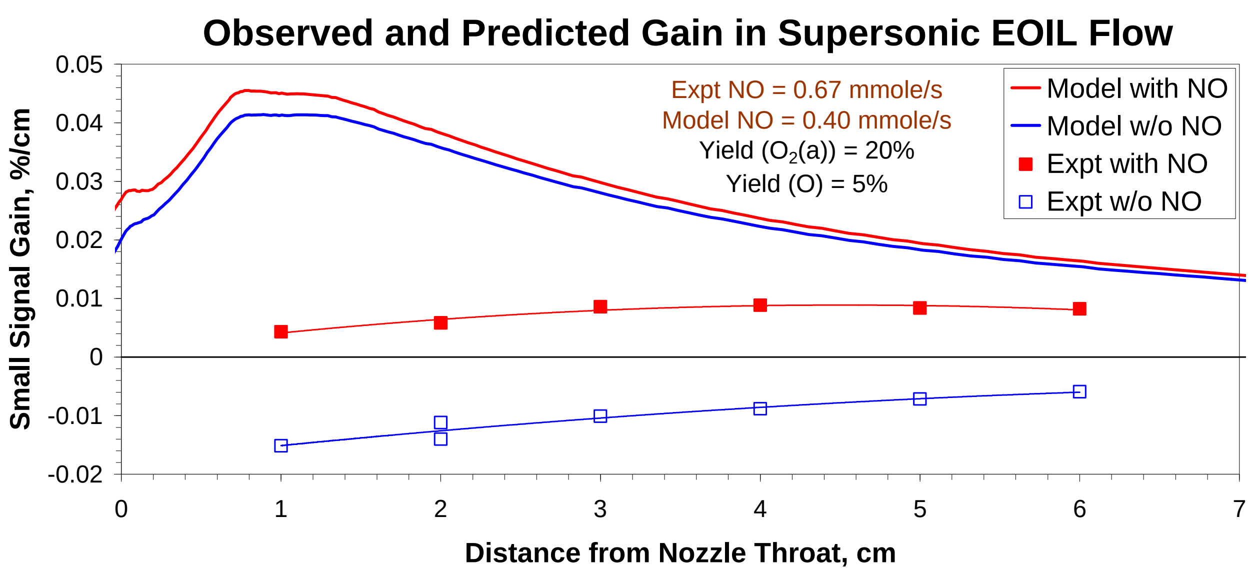
- **Chemically rich, energetic, reacting flow with competing phenomena**
  - Multispecies detection required
  - COIL, EOIL: O_2(a,b), I*, I, I_2, gain, T, O, O_3
  - DPAL, XPAL: ground-state M, numerous M*, M_2*, MX*, gain

- **Objective: detect key species concentrations vs. flow time**
  - Vary operating conditions systematically
  - Quantify species production and loss rates
  - Relate to system design requirements

- **Put a "cage" around the model:**



Electric Oxygen Iodine Laser (EOIL)

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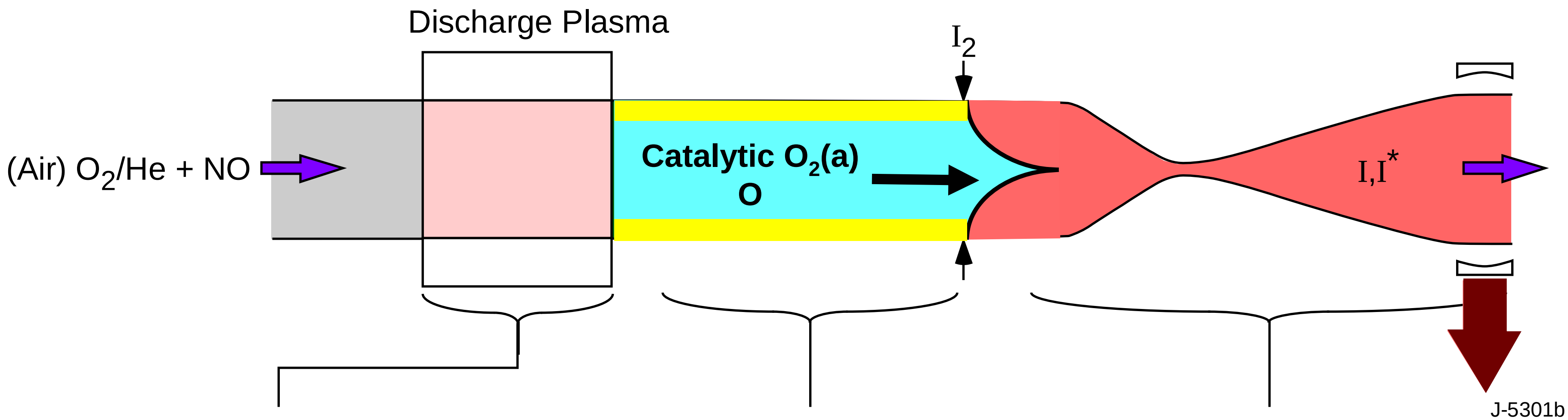

$$e^- + O_2 \rightarrow O_2(a) + e^-$$

$$e^- + O_2 \rightarrow O + O + e^-$$

Ionization

$$e^- + O_2(a) \rightarrow \text{losses}$$

Dilution in He required

$$O + NO + M \rightarrow NO_2 + M$$

$$O + NO_2 \rightarrow NO + O_2$$

$$O + O_2 + M \rightarrow O_3 + M$$

$$O + O_3 \rightarrow O_2 + O_2$$

$$NO + O_3 \rightarrow O_2 + NO_2$$

$$O + I_2 \rightarrow IO + I$$

$$O + IO \rightarrow O_2 + I$$

$$\boxed{O_2(a) + I \rightleftarrows O_2 + I^*}$$

$$O + I^* \rightarrow O + I$$

$$I^* + O_2 \rightarrow I + O_2(v)$$

$$\frac{[I^*]}{[I]} \rightarrow K_{EQ}(T)\frac{[O_2(a)]}{[O_2]}$$

Hybrid EOIL: Catalytically enhanced $O_2(a)$

PSI Microwave Discharge Flow Reactors
(2450 MHz)

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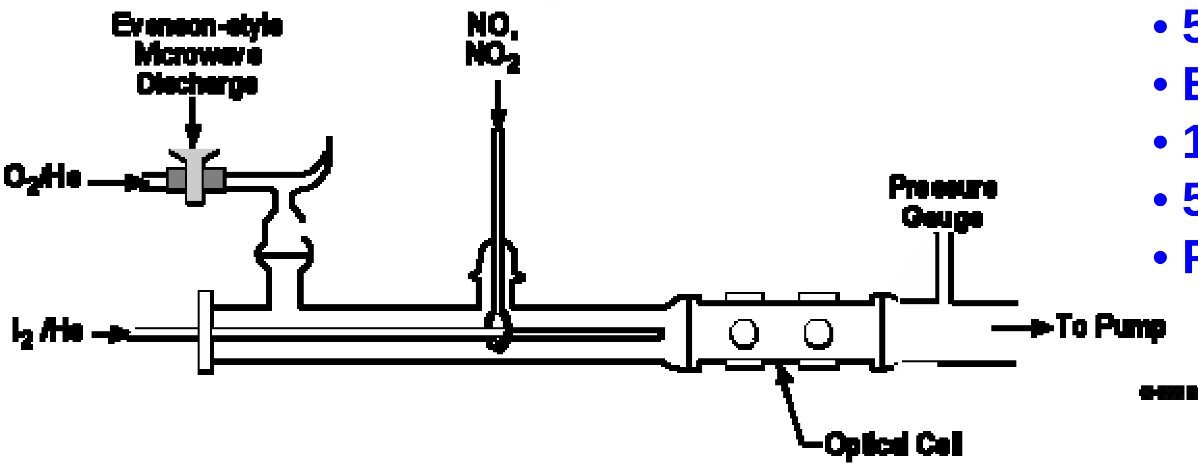
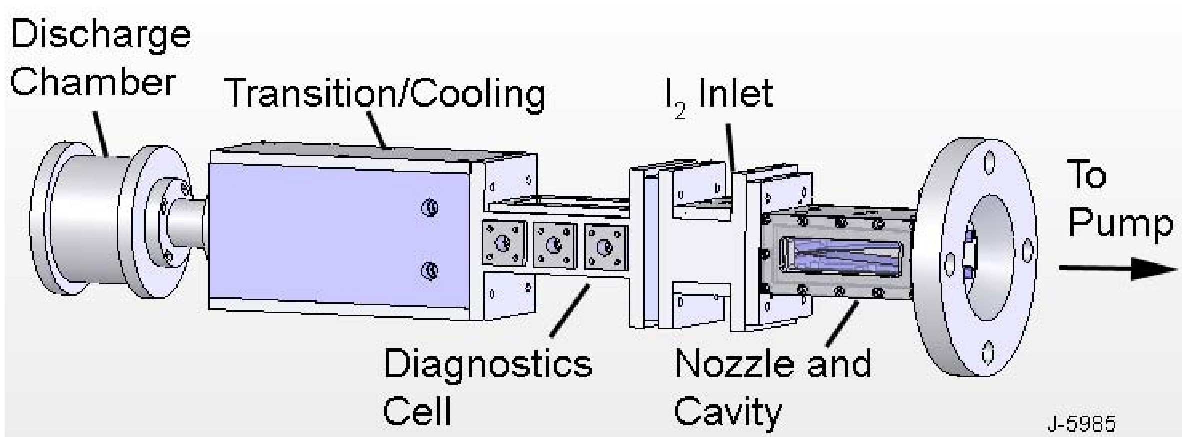
Low-Pressure Reactor: Active-O_2 Kinetics



- 50-100 W, 10-100 Td
- External cavity discharge
- 1-10 Torr, 1-5 mmole/s
- 5-cm i.d. Pyrex flow tube
- Flow T ~ 300-350 K

EOIL Subsonic/Supersonic Reactor

- 1-5 kW, 10-50 Td
- Coaxial MIDJet discharge
- 30-70 Torr, 40-100 mmole/s
- M ~ 2 supersonic cavity
- Lasing typically 100-150 mW
  -- $M^2 = 1.08 \pm 0.01$



Near-IR Absolute Emission: O_2(a) and I*

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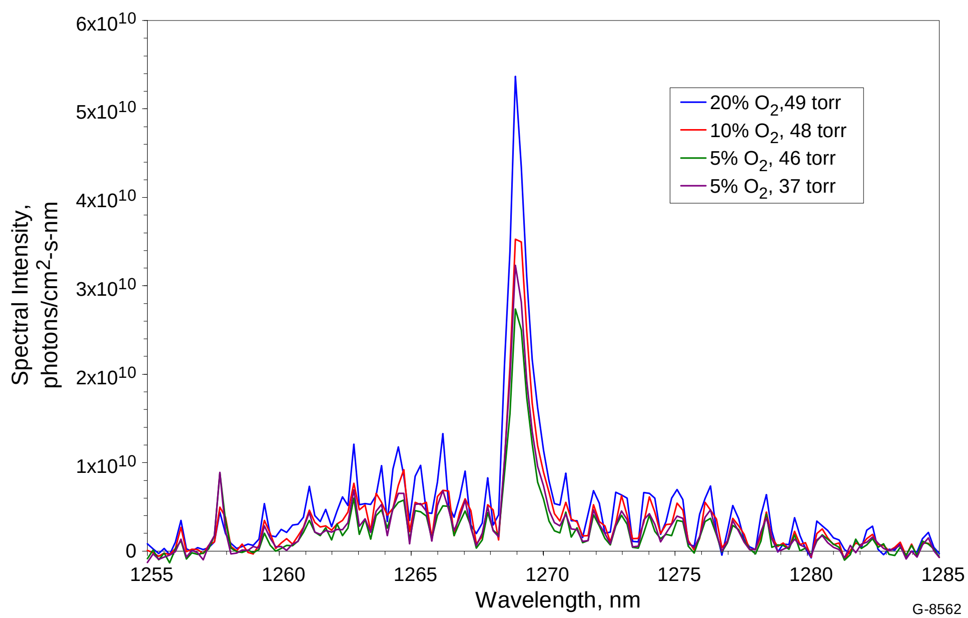
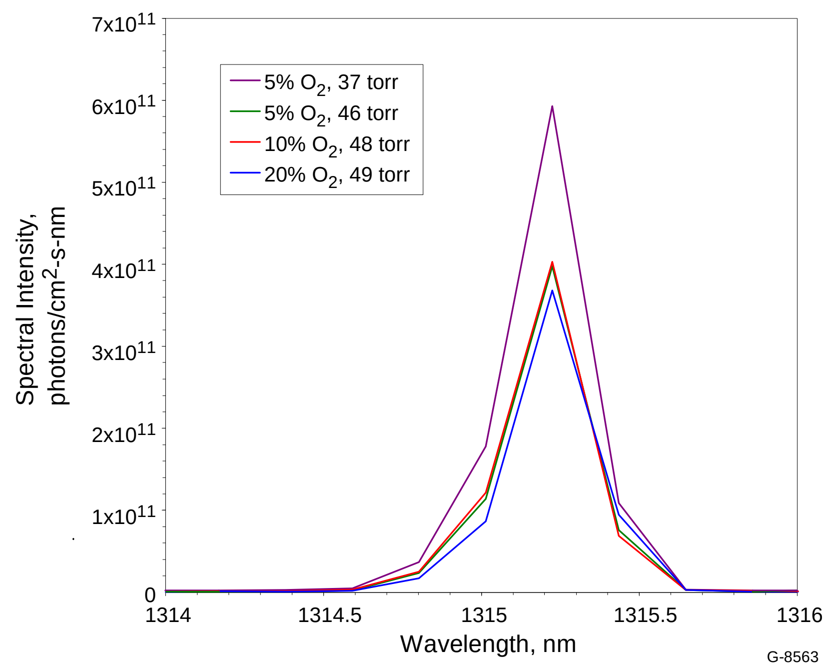
- **InGaAs array – monochromator: observe entire band**
- **Concentration = Intensity ÷ Einstein coefficient**

$O_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$



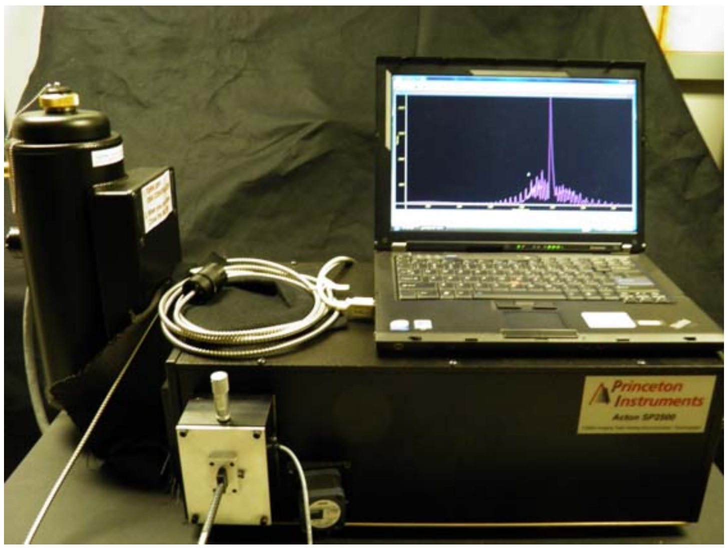
- **A_{00} = 2.20 x 10^{-4} s^{-1} (±10%)**
- **Detection limit ~ 5 x 10^{12} cm^{-3} (5 cm path)**

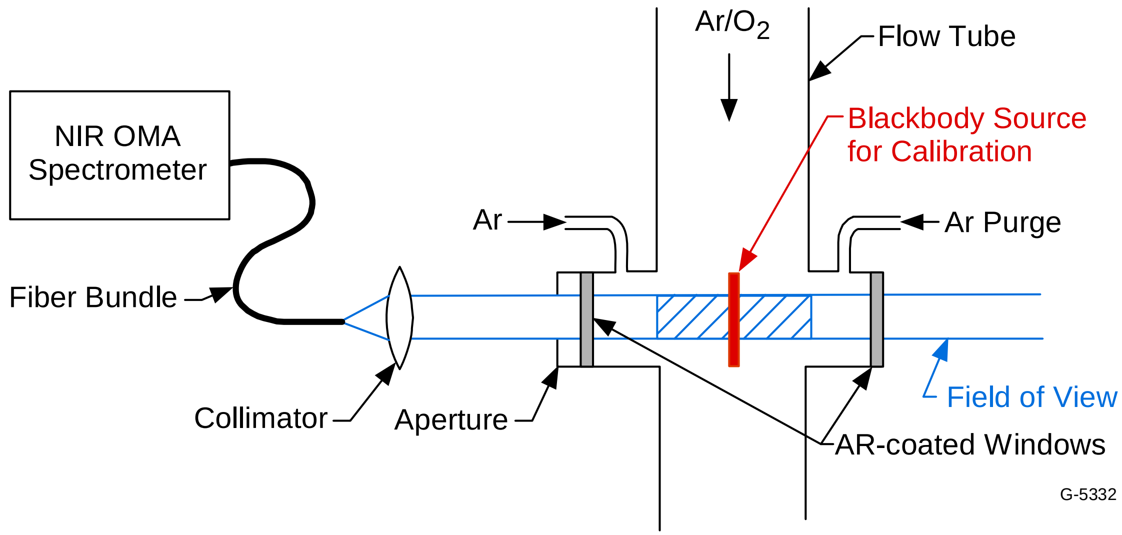
$I(^2P_{1/2} \rightarrow {}^2P_{3/2})$



- **A = 8.0 s^{-1} (±20%)**
- **Detection limit ~ 10^8 cm^{-3} (5 cm path)**

NIR Photometric Calibration: $O_2(a)$ and I^* Emission





- **Collimated field of view: no reflective surfaces**
  - Eliminate stray light, e.g. discharge emission
- **Etendue (AΩ) for calibration is identical to that for volume emission**
- **Spectral responsivity = (signal) / (Planck function)**
- **Blackbody calibrations 800-1000º C agree within 1%**

Principle of Absolute Calibration Method

- **Instrumental signal for both blackbody and $O_2(a \rightarrow X)$ emission:**
  - $S(\lambda) = F(\lambda)\ T(\lambda)\ A\Omega\ \delta\lambda\ I(\lambda)$ F = spectral responsivity
  - Use the same $\{A\Omega\ \delta\lambda\}$ for calibration and gas emission measurements
- **Determine F by measuring blackbody spectrum (Planck function):**
  - $F(\lambda) = S_{BB}(\lambda) / N(\lambda, T_{BB})$ $T_{BB} \sim 1000$ C
  - Area of source > area of fov
  - Accuracy <1%
- **Gas radiance in photons/cm^2-s-sr-nm:**
  - $I_{aX}(\lambda) = S_{aX}(\lambda) / \{F(\lambda)\ T(\lambda)\}$
  - Correct for spectral baseline/background
- **Determine $O_2(a)$ concentration from spectrally integrated intensity:**
  - $[O_2(a)] = (4\pi/\ell) \int I_{aX}(\lambda) d\lambda / A_{aX}$ A_{aX} = Einstein coefficient

Spectral Fitting Analysis: $[O_2(a,v)]$, T_{rot}

- **$O_2(a^1\Delta_g \rightarrow X^3\Sigma_g^-)$ spectroscopy:**
  - Magnetic dipole transition
  - Hund's coupling case (b)
  - Bose-Einstein statistics ($^{16}O_2$)
  - ➔ 9 rotational branches

- **Our procedure: determine line strengths for (0,0) from line-by-line compilation (HITRAN)**
  - Boltzmann rotational temperature
  - Shift (0,0) envelope to band centers for (1,1), (2,2), etc.

- **Convolve with instrument scan function**
  - Triangular slit function for grating monochromator (0.3 nm FWHM)

- **Linear least squares solutions are $\{[O_2(a,v)]\}$**

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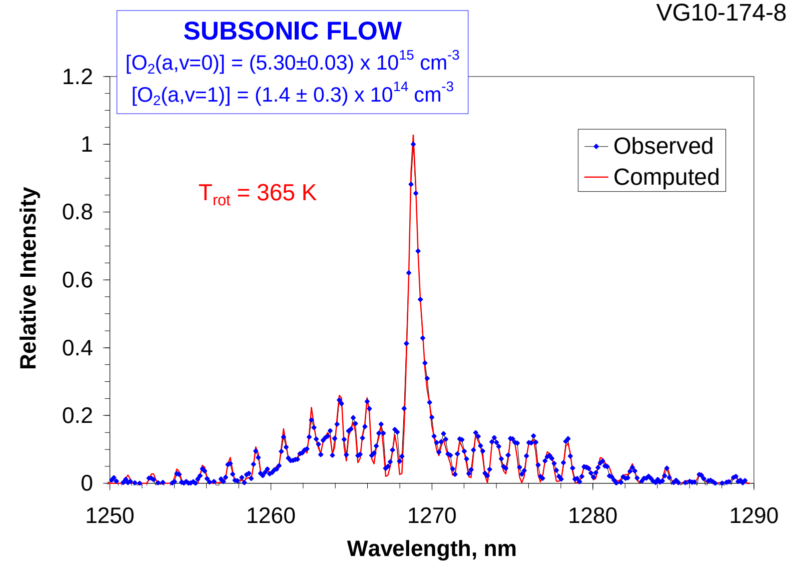

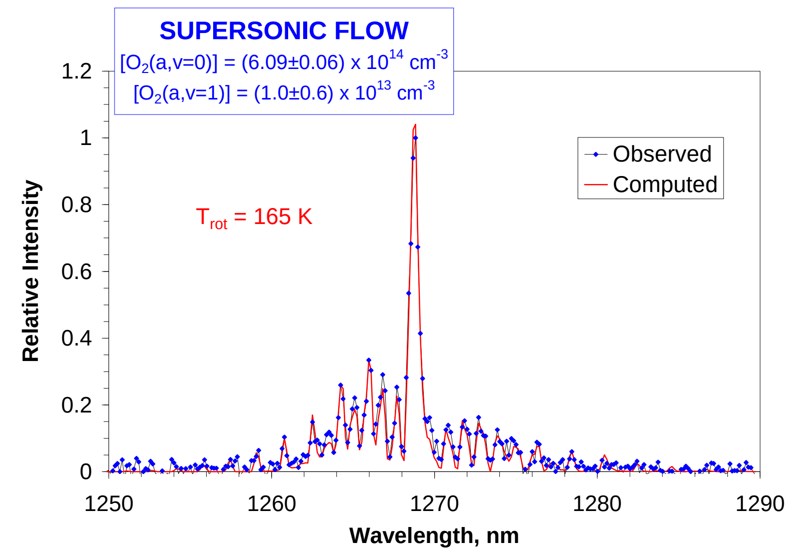

Estimation of A_{11}, A_{22}, A_{33} Values

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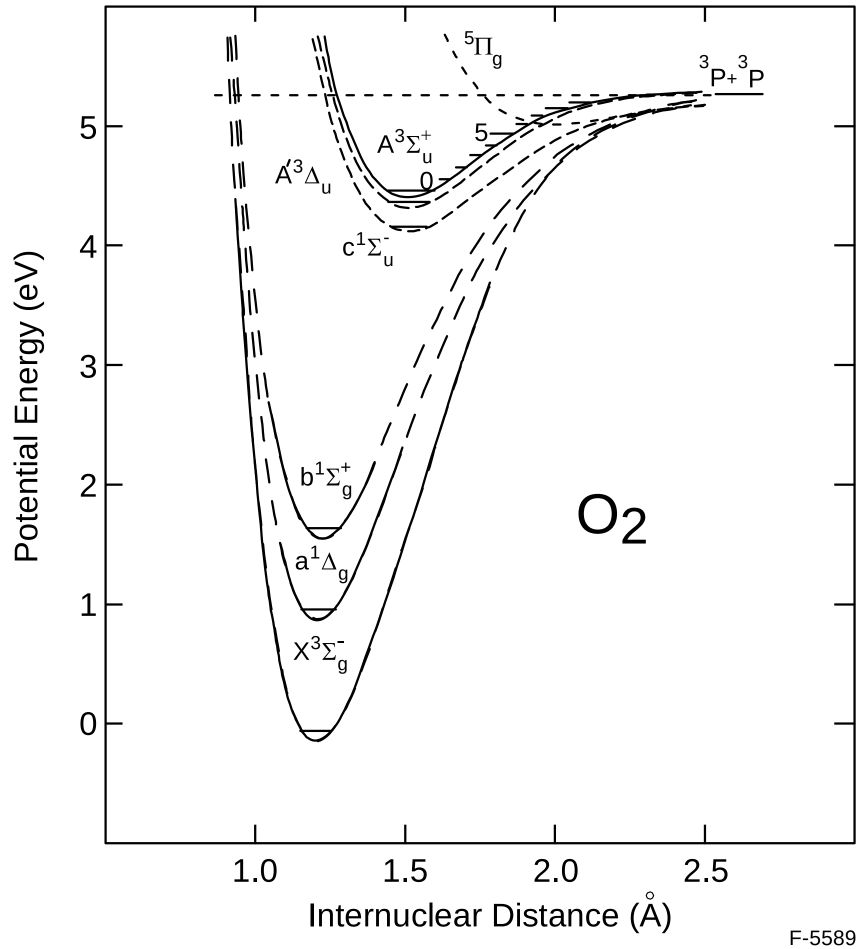
- **Scale values from A_{00} via Franck-Condon factors, transition moment vs. r-centroid:**

  $$A_{v'v''} = (64\pi^4/3h)\,(\nu^3 q_{v'v''})\,(R(r))^2$$

- **Franck-Condon factors, r-centroid values from Krupenie (1972)**

- **Estimate scaling of $(R(r))^2$ from $A_{00}:A_{01}:A_{10}$**
  - Literature: A_{00}/A_{01} is either ~50 or ~80
  - **PSI measurement: $A_{00}/A_{01} = 52 \pm 6$**
  - Badger et al. (1965): $A_{00}/A_{10} > 200$
  - Solution: $(R(r))^2$ varies slightly with v'

- **Solutions for $A_{00} = 2.20 \times 10^{-4}\ s^{-1}$:**
  $A_{11} = 2.17 \times 10^{-4}\ s^{-1}$
  $A_{22} = 2.12 \times 10^{-4}\ s^{-1}$
  $A_{33} = 2.06 \times 10^{-4}\ s^{-1}$



BUT WE DO NOT OBSERVE O_2(a,v>0)!

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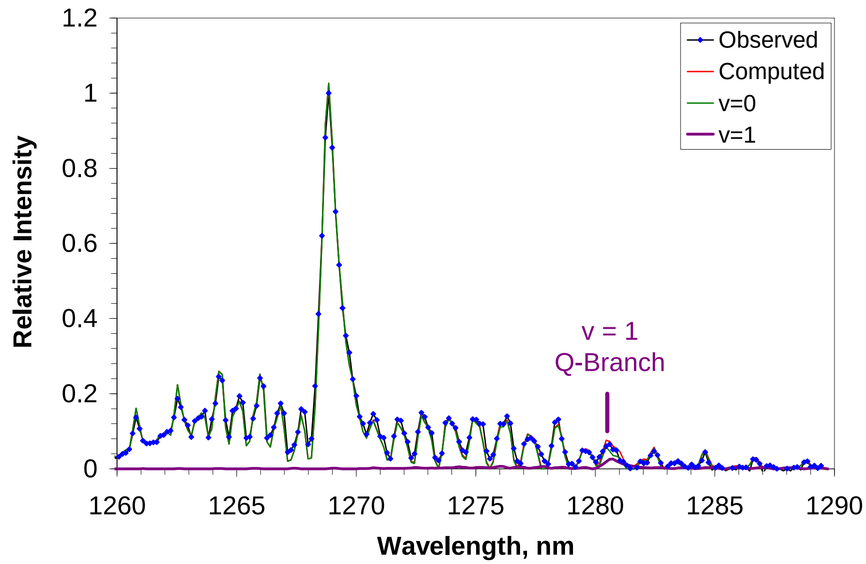

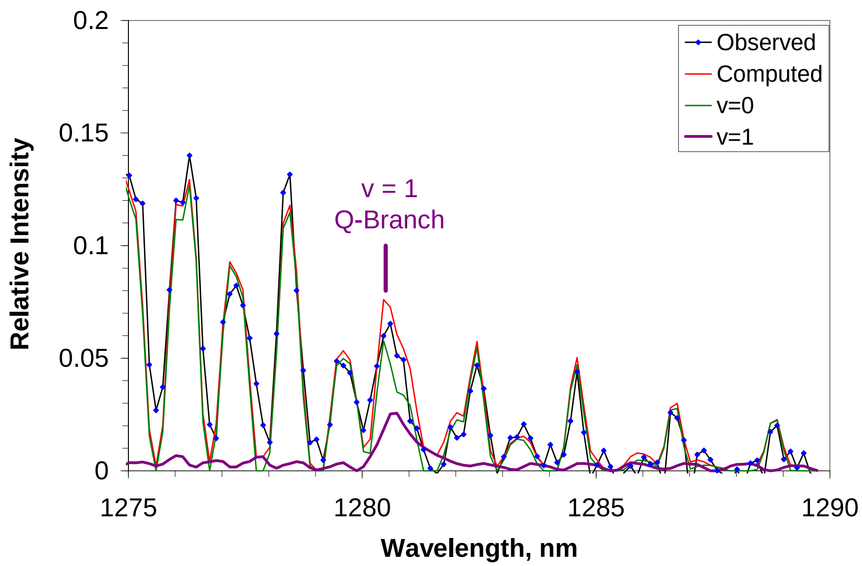

- **Typical fits: [(v=1)]/[(v=0)] ~ 3 to 7 %**
  - Tends to track with temperature of discharge, i.e. thermal populations only
- **True for large range of conditions:**
  - 50 W – 2 kW discharges
  - 0.5 – 50 Torr
  - Cl_2/BHP generators, energy pooling conditions
- **Slanger, Copeland 2003: O_2(a,v) exchange with O_2(X, v=0) is fast**
- **Implications for COIL I_2 dissociation mechanism?**

Spectral Fitting vs. Integration

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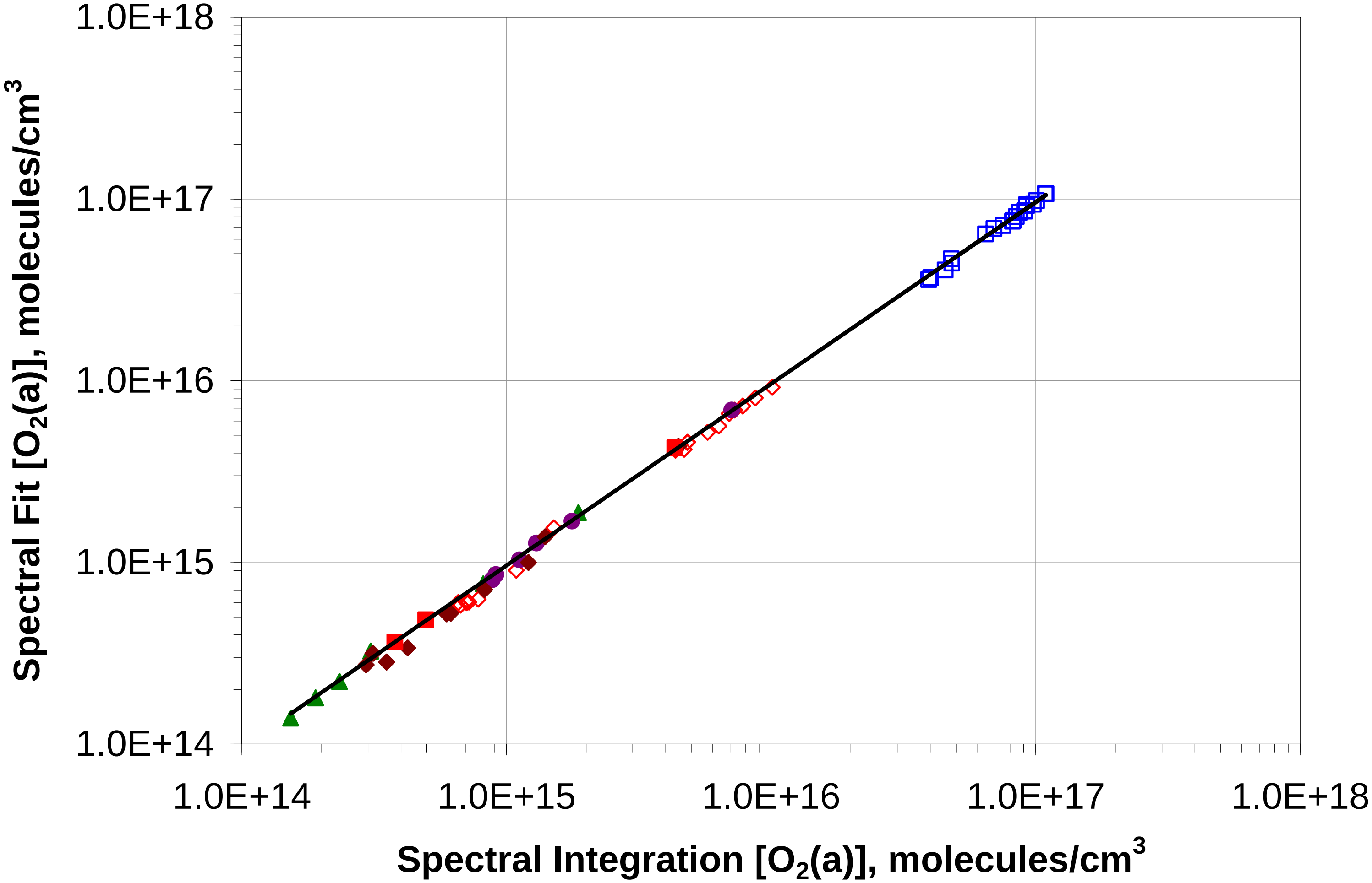

- **Philosophy: spectral fitting confirms band shape, T_{rot}, T_{vib}, no other radiators; then integration gives accurate values**

Air Afterglow: O + NO → NO_2 + hν

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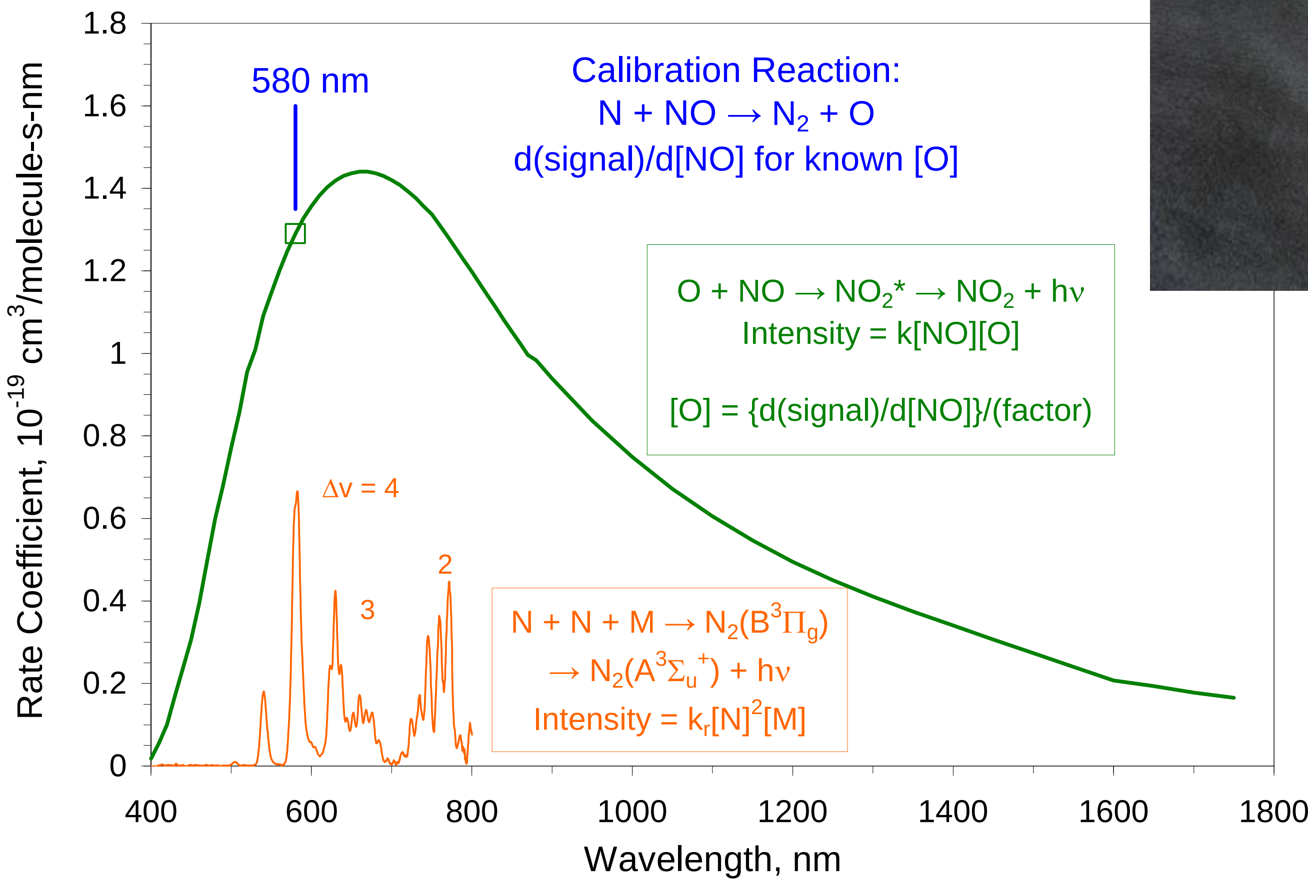
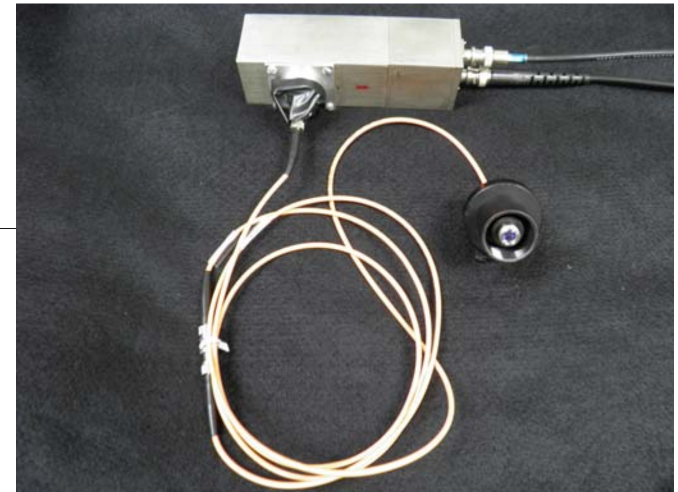
- **Fiber-coupled photomultiplier**
  - **-- 580 nm filter, collimated field-of-view**
- **Calibrate with blackbody <u>and</u> titration reaction**





J. Phys. Chem. <u>90</u>, 320-325 (1986)

- **Calibrations allow measurement of absolute emission rates for known [O], [NO]**
- **→ Determination of k(580 nm)**
- **Scale to other wavelengths via relative intensity measurements**

Air Afterglow: Determination of [O]

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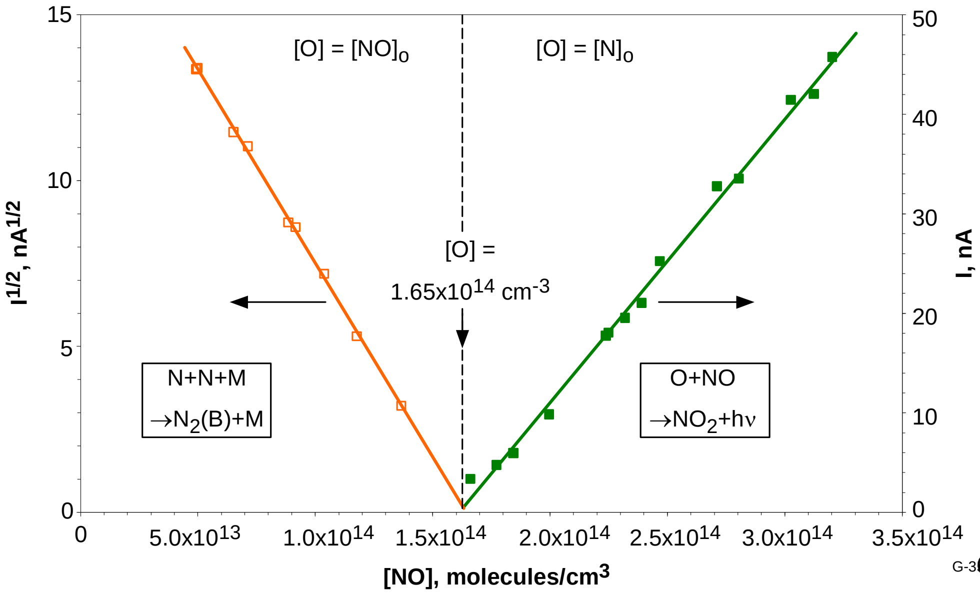
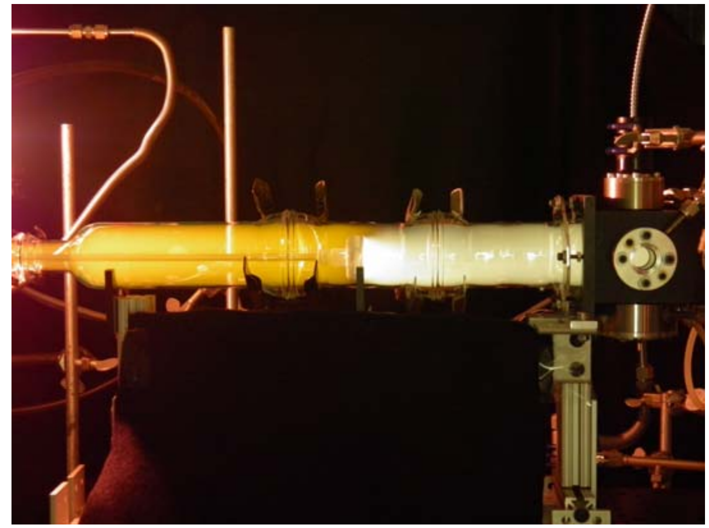




N_2 **Discharge:** $N + NO \rightarrow N_2 + O$

$O + NO \rightarrow NO_2 + h\nu$

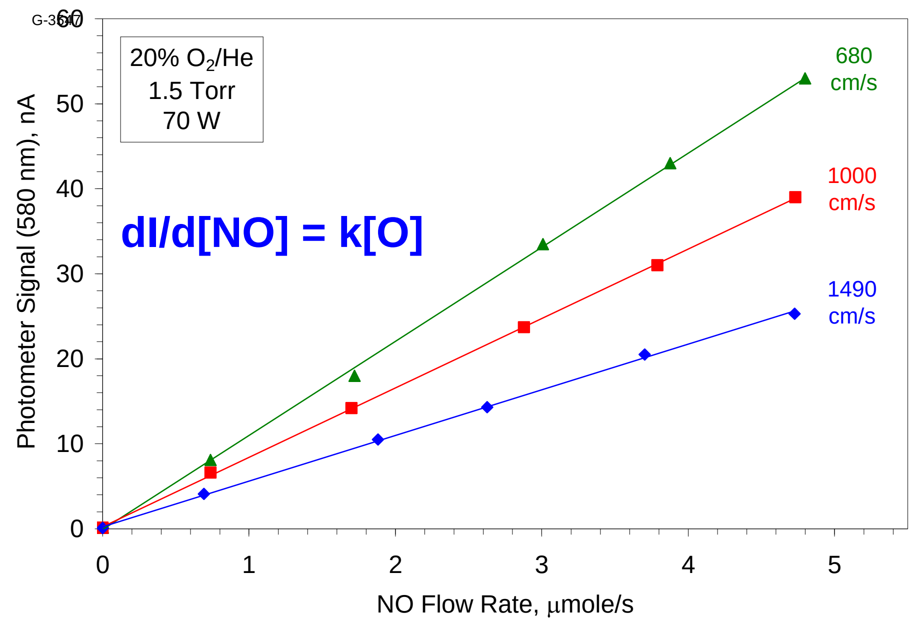
For [NO] < [N]: $N_2(B\rightarrow A)$ **emission**

For [NO] > [N]: O + NO emission

slope ÷ [O] = calibration factor

correct for O+NO+M reaction

Blackbody calibration: $\rightarrow k_{580}$



Measurements: Discharge Production of O, $O_2(a)$

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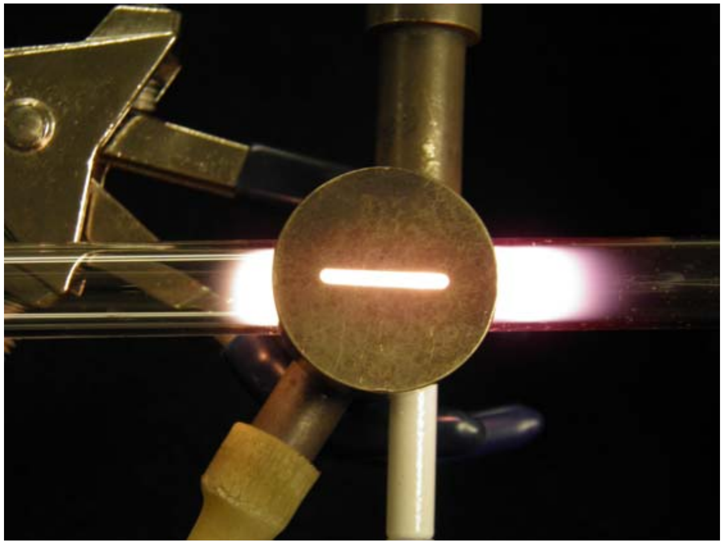

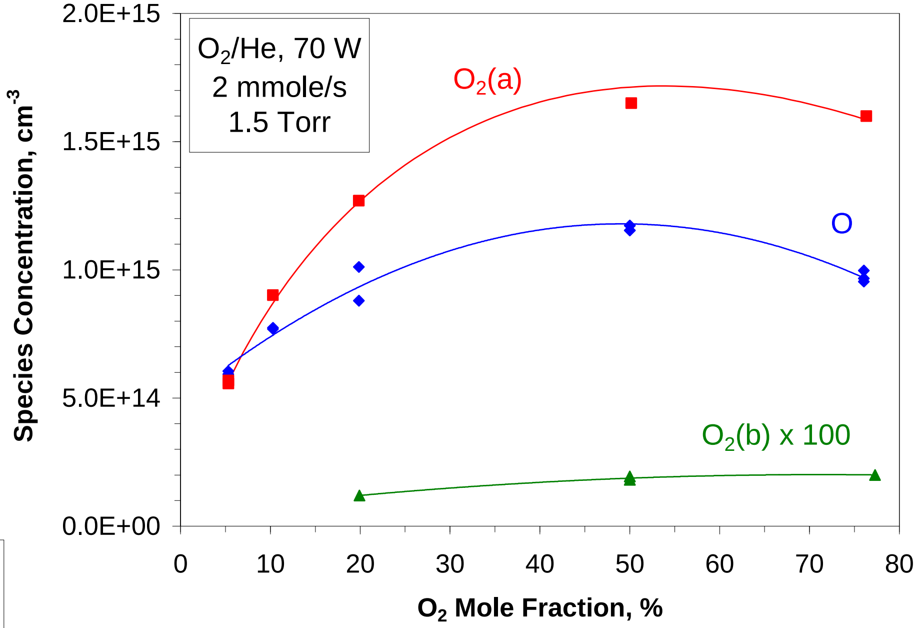

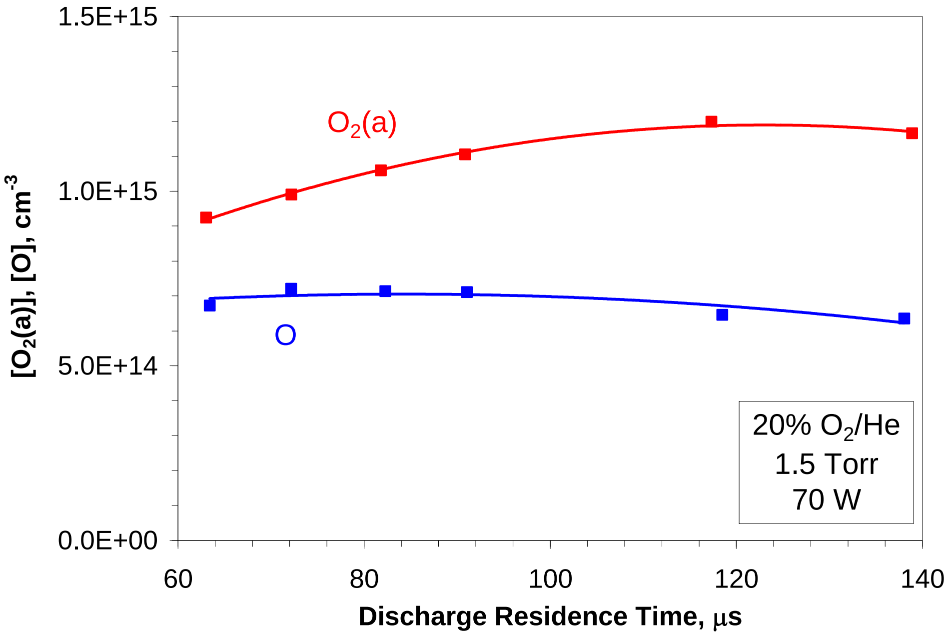

- **Observed $[O]/[O_2(a)]$ is ~ 1 or less**
- **Discharge models predict $[O] >> [O_2(a)]$**
  - **Electron-impact O_2 dissociation cross sections are too large**
  - **Possible O loss on hot walls**

Ultrasensitive Dual-Beam Absorption: O_3 and I_2

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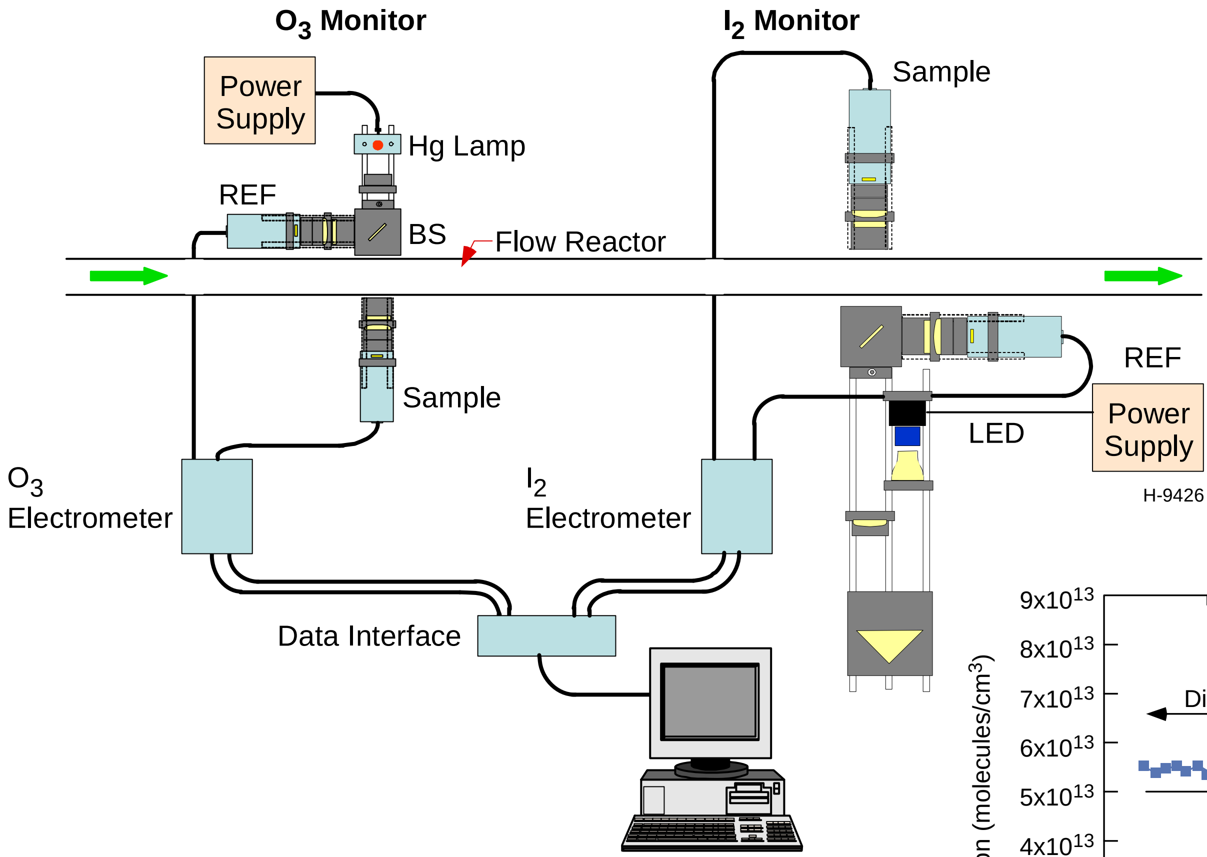
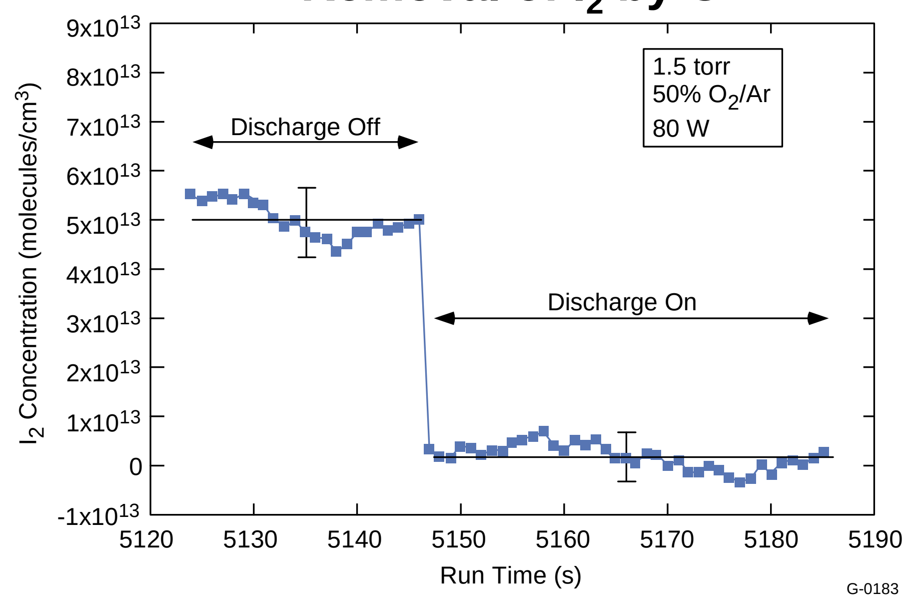


Absorbance = $\ln(I_o/I) = \sigma N \ell$

Detection limit ~ 10^{-5}

Removal of I_2 by O



$\sigma(I_2)$ = 1.64 x 10^{-18} cm^2, 488 nm

$\sigma(O_3)$ = 1.14 x 10^{-17} cm^2, 254 nm

O_3 Formation in Active-Oxygen Flow

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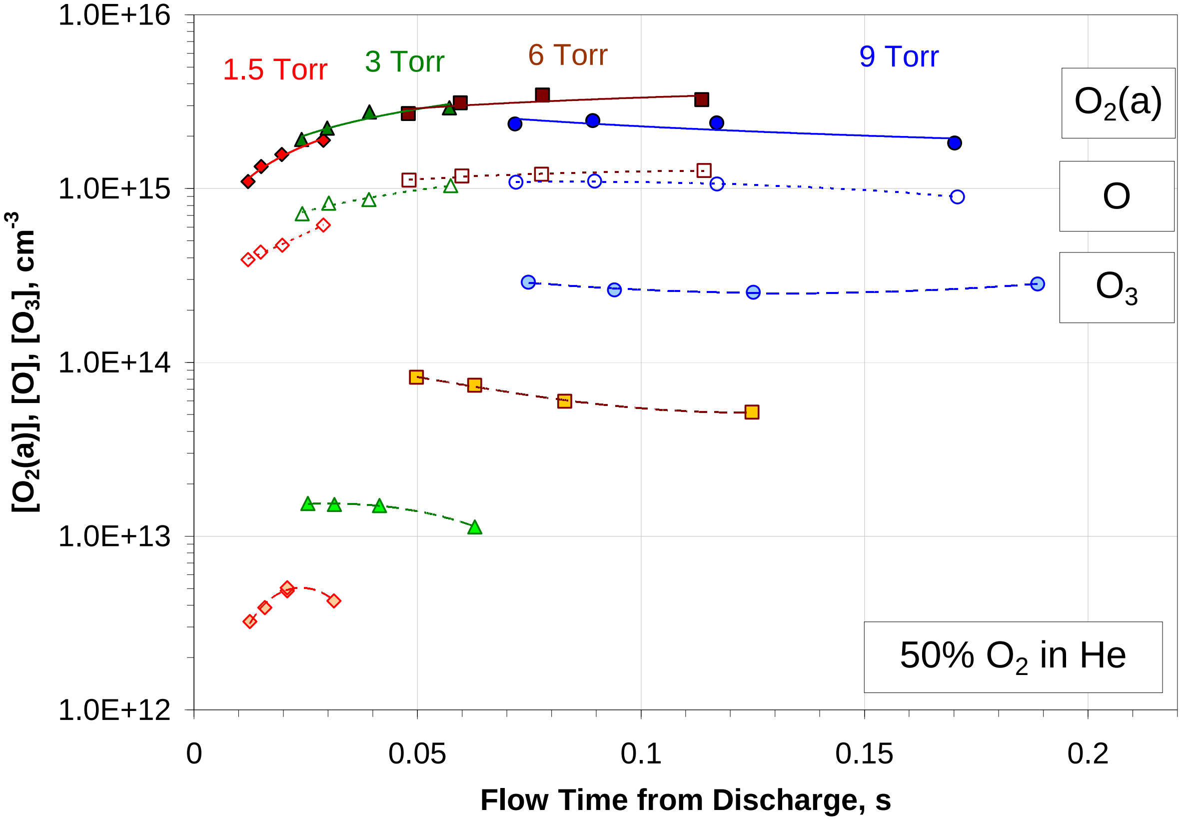


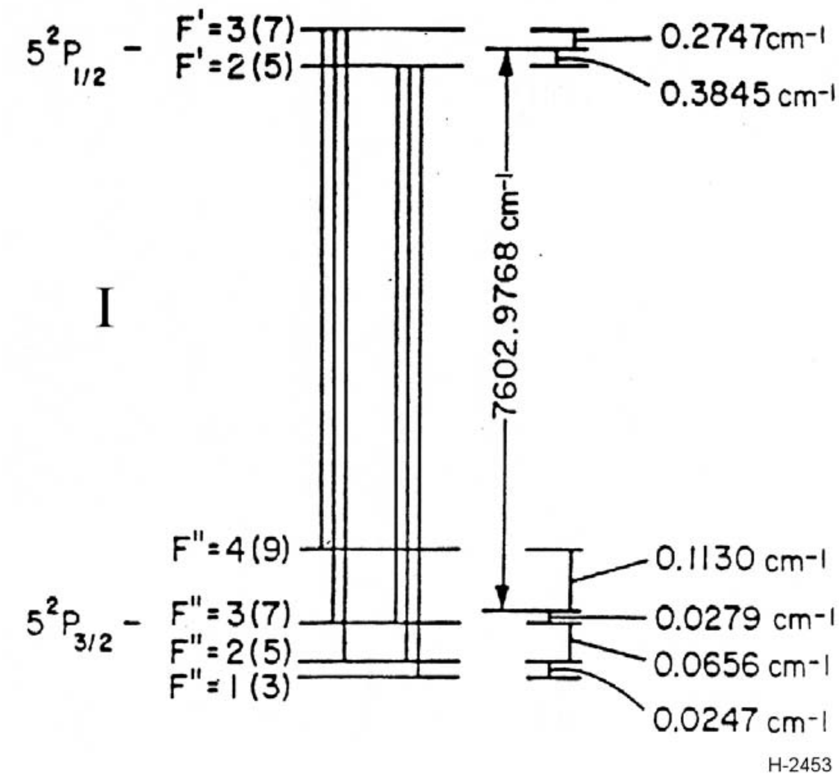
- **Surprise: O and O_3 are in ~ steady state!**
  - **Requires O_3 conversion to O**

$$O + O_2 + M \rightarrow O_3(v) + M$$

$$O_2(a) + O_3(v) \rightarrow O + 2O_2,\ k = 5 \times 10^{-11}\ cm^3/s$$

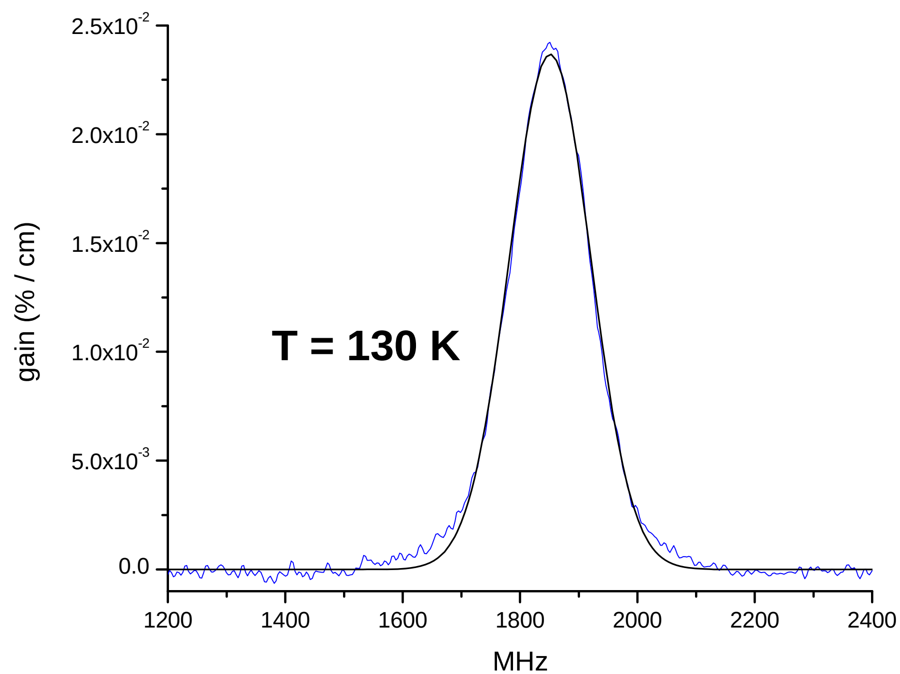
J. Chem. Phys. 87, 5209-5221 (1987)

Small Signal Gain: Atomic Iodine



- Probe transmission on (3,4) line
- $G/\sigma(T) = [I^*] - [I]/2$
- [I*] from IR emission
  → [I], [I*]/[I], ([I*]+[I])/2

- Scanning tunable diode laser
- Balanced ratiometric detection
- Detection limit ~10^{-5} %/cm
- Doppler width → temperature
- Method widely used for COIL, EOIL development



Observations of I*/I Behavior

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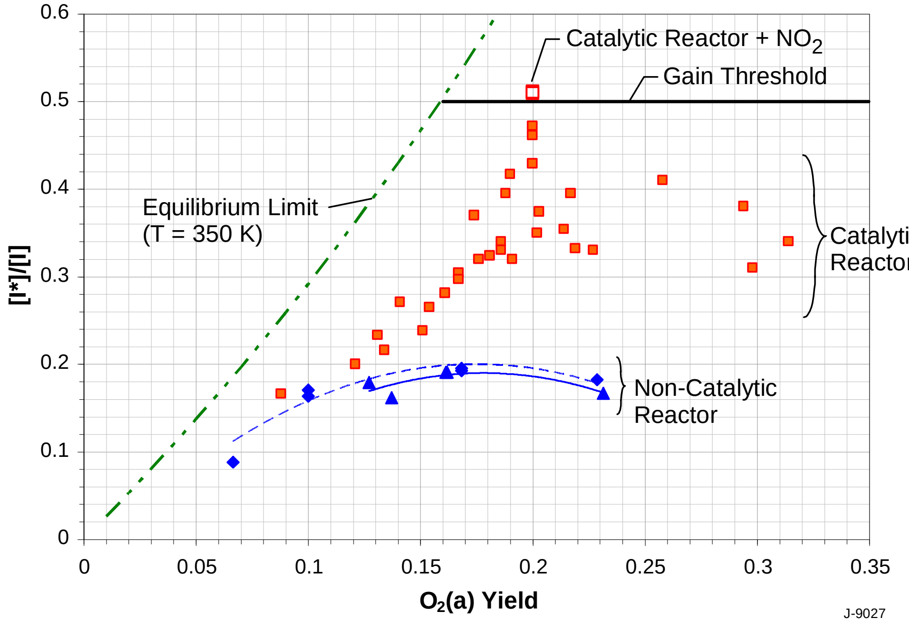
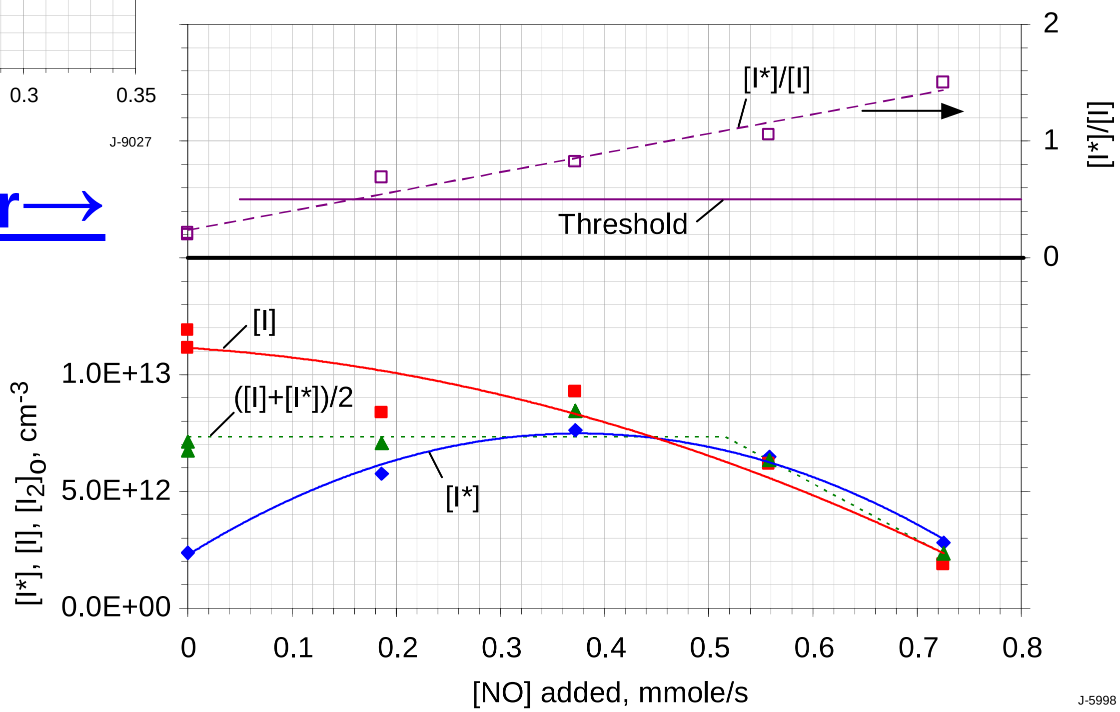


←Subsonic flow reactor

- **I*/I ratio is limited by I* loss reaction**
- **Catalytic environment enhances attainable I*/I**
- **Chem. Phys. Lett. 469, 68-70 (2009)**
  Proc. SPIE 7196-04 (2009)
  Proc. SPIE 7581-06 (2010)

Supersonic flow reactor→

- **I*/I ratio is limited by I* loss reaction**
- **Addition of NO enhances I*/I**
- **I*/I continues to increase past optimum gain point**
- **Proc. SPIE 6874-10 (2008)**
  Proc. SPIE 7581-03 (2010)
  J. Appl. Phys. D 43 025208 (2010)



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Application to Alkali and Alkali-Exciplex Systems

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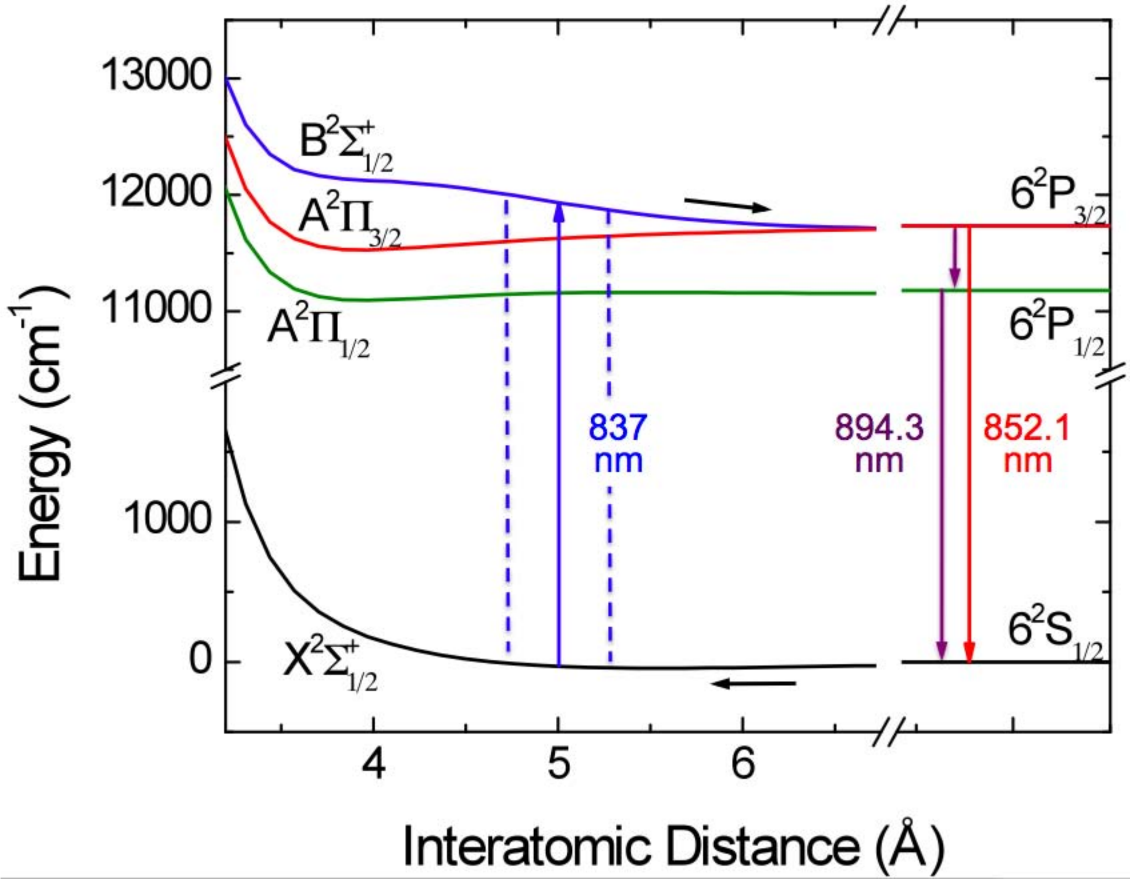
Cs-Ar Potential Energy Diagram



- **DPAL: pump D_2, lase D_1 (C_2H_6 promotes spin-orbit transfer)**
- **XPAL: pump broadband exciplex X→B, lase on D_1 or D_2**

DPAL/XPAL Gain Measurement Test Bed
(Diode laser scanning D_1 line)

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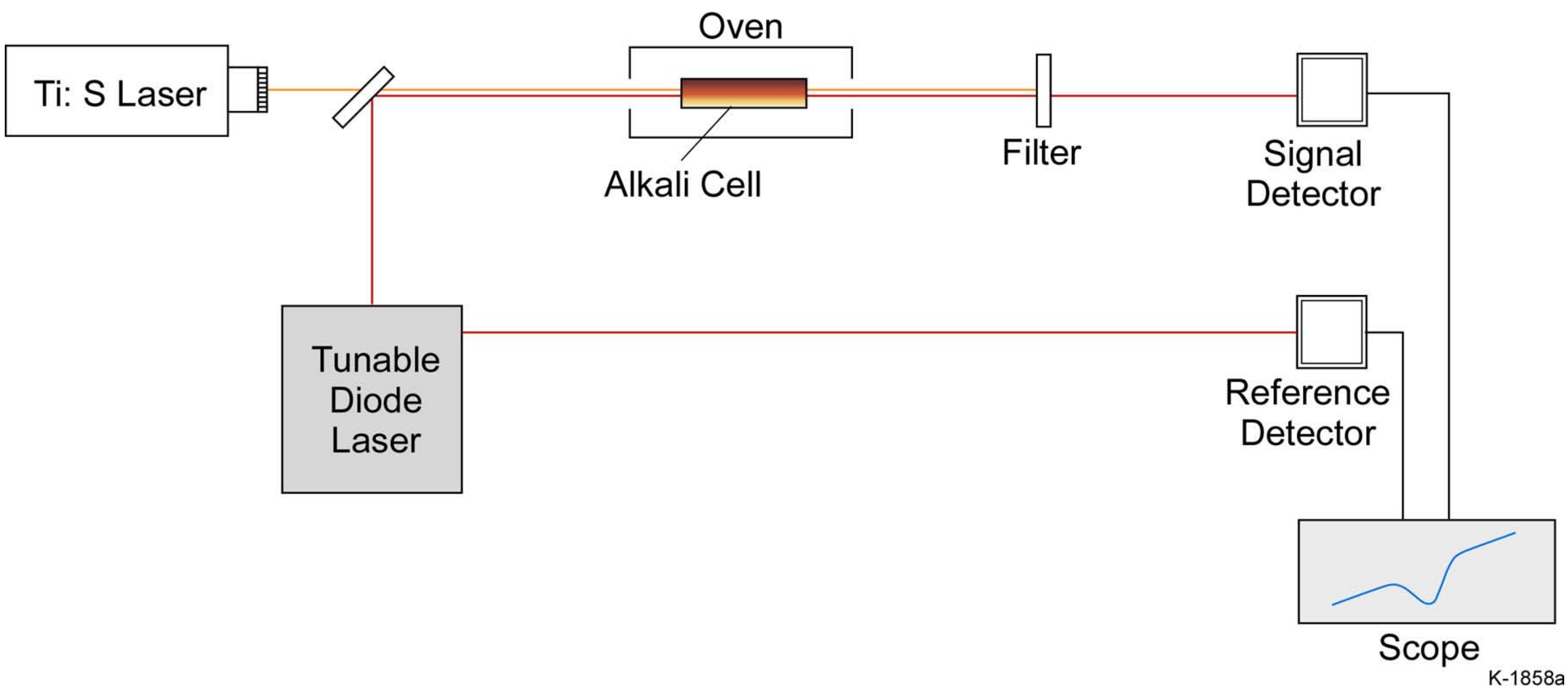

- Direct probe of population inversion dynamics
- Aids in design of optical resonators
- Portable: take to other facilities
- Can extend to spatial imaging of gain
  - Expect significant spatial effects in power scaling
  - Valuable tool for scaling DPAL to high powers

Optical Layout for DPAL/XPAL Gain Measurements

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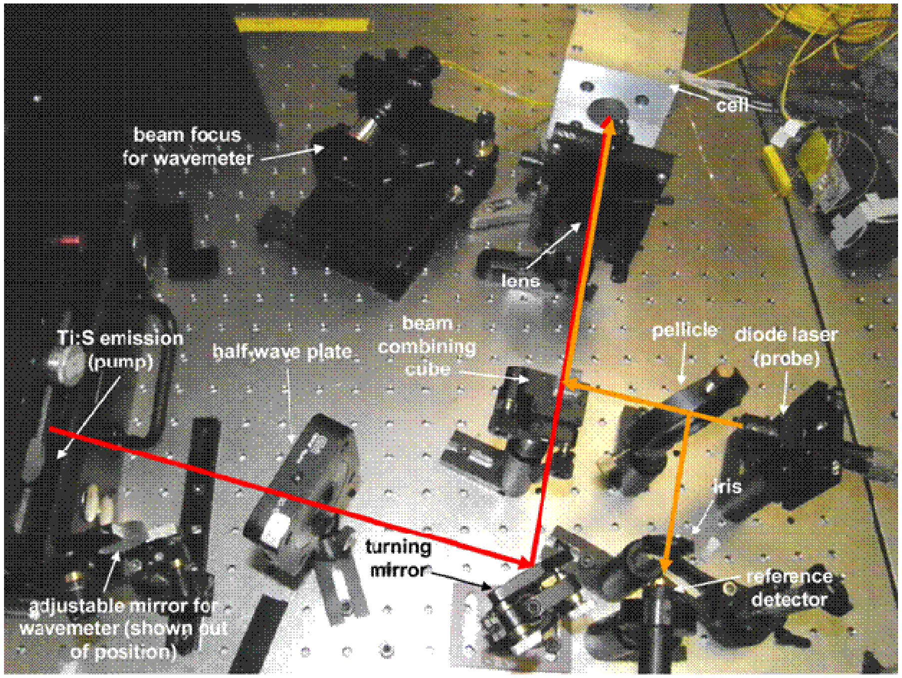

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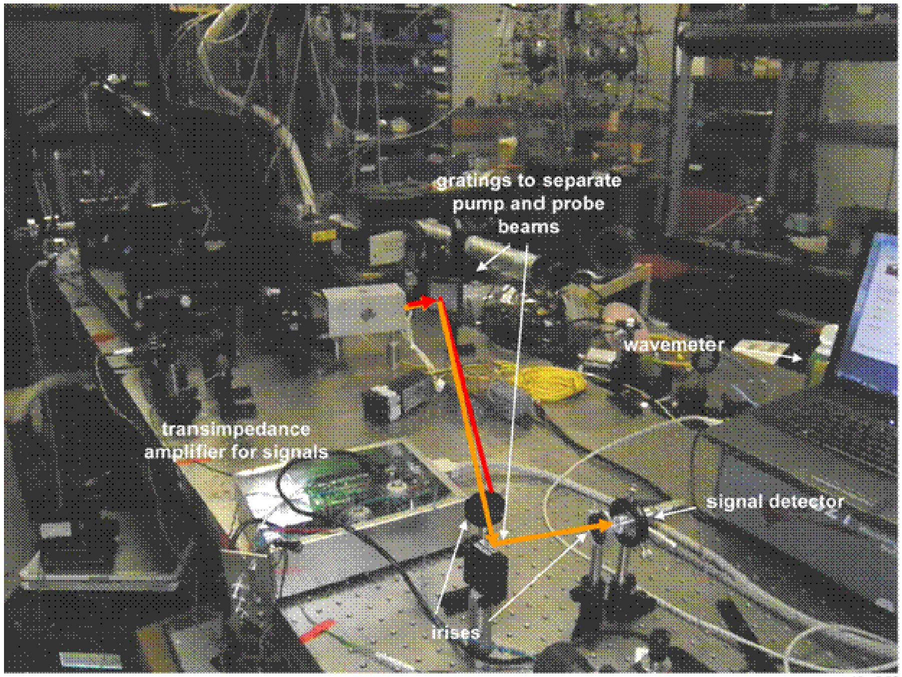

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Computed D_1 Absorption Spectra: Cs

Collisional Broadening Effect

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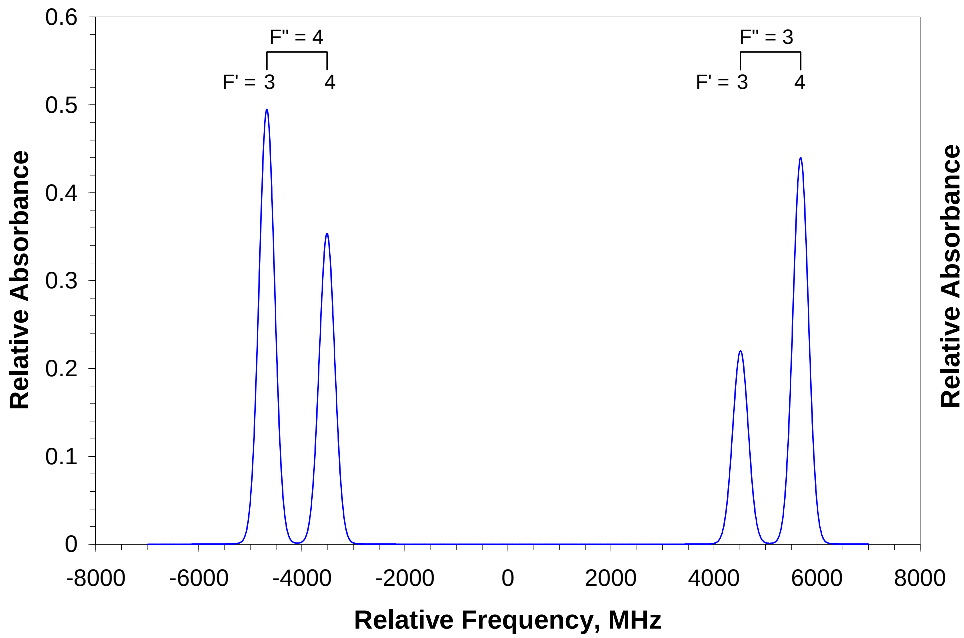
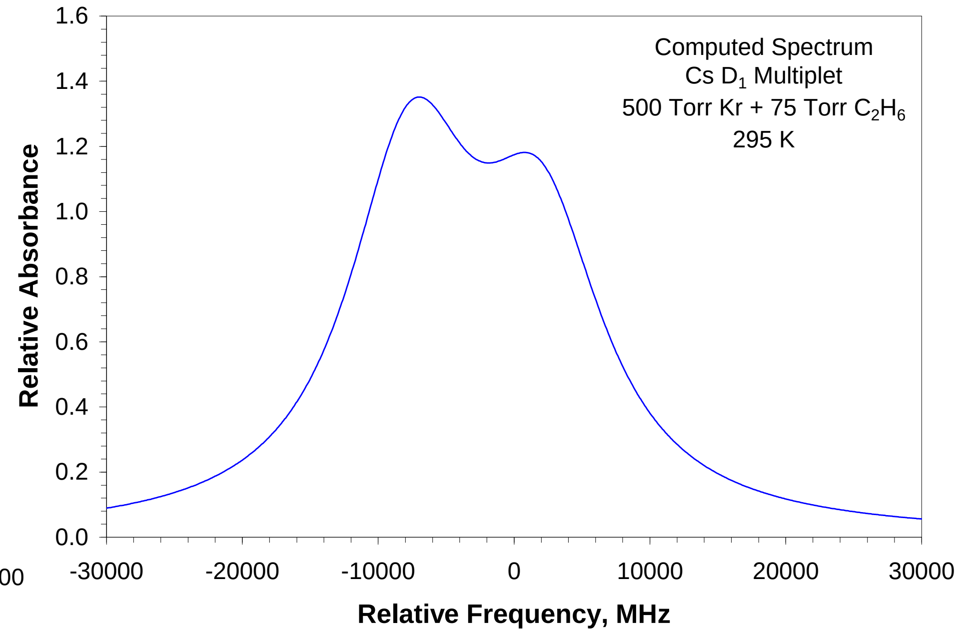
Cs $^2S_{1/2}$ – $^2P_{1/2}$, 894 nm

Low Pressure, Doppler broadening



High Pressure, collisional broadening



- **Collisional broadening greatly expands required scan range**
- **High optical thickness at elevated temperatures**

Absorption/Gain Spectra: $Cs(^2S_{1/2}, F''=4 \rightarrow ^2P_{1/2}, F')$, 894 nm

500 Torr Kr + 75 Torr C_2H_6, 338 K

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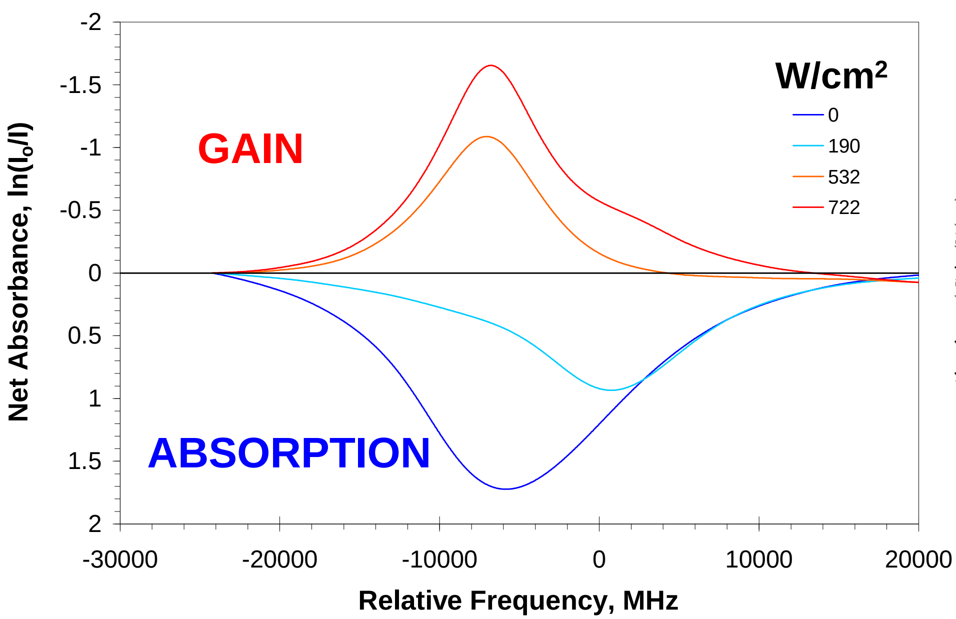
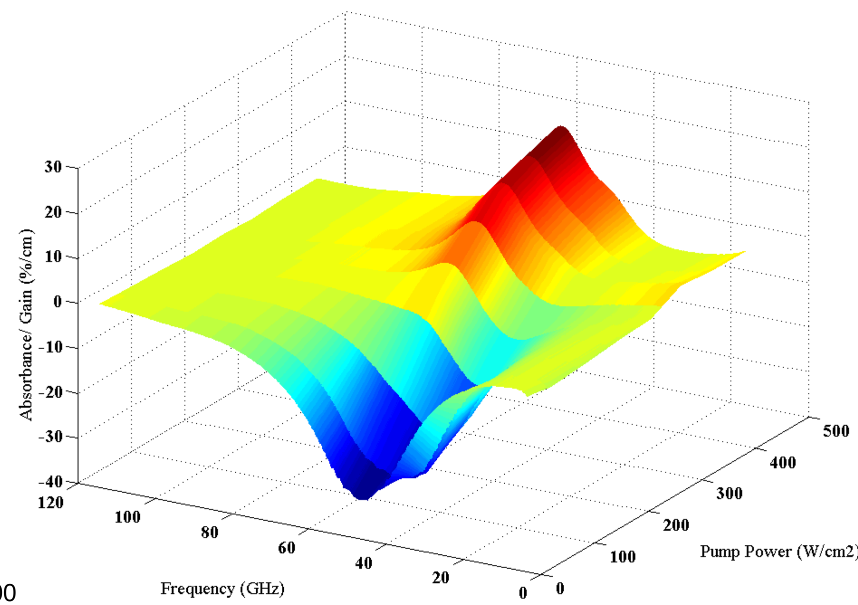
Pump Laser: $^2S_{1/2} \rightarrow ^2P_{3/2}$, 852 nm



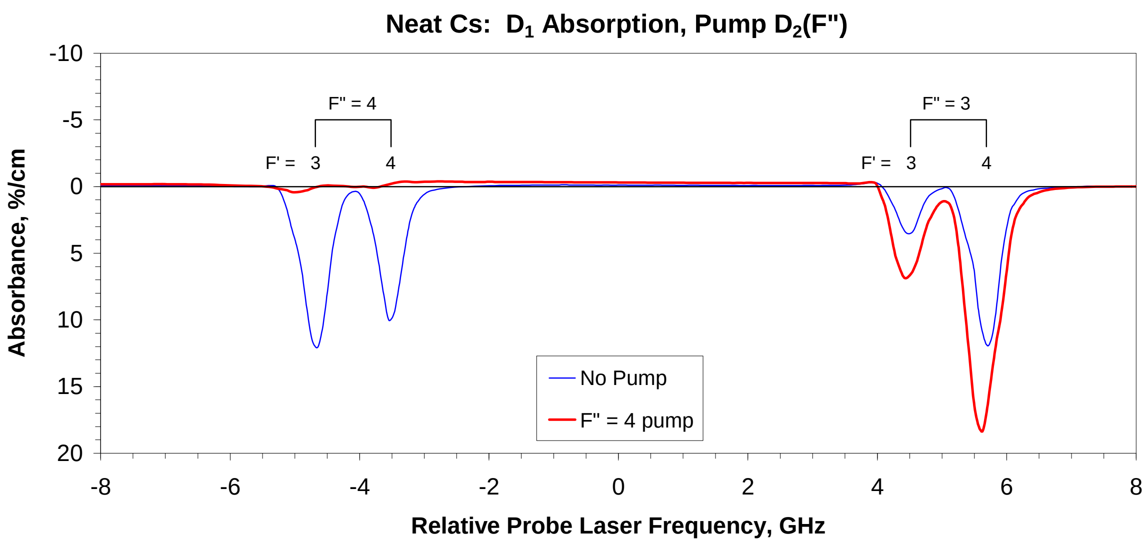


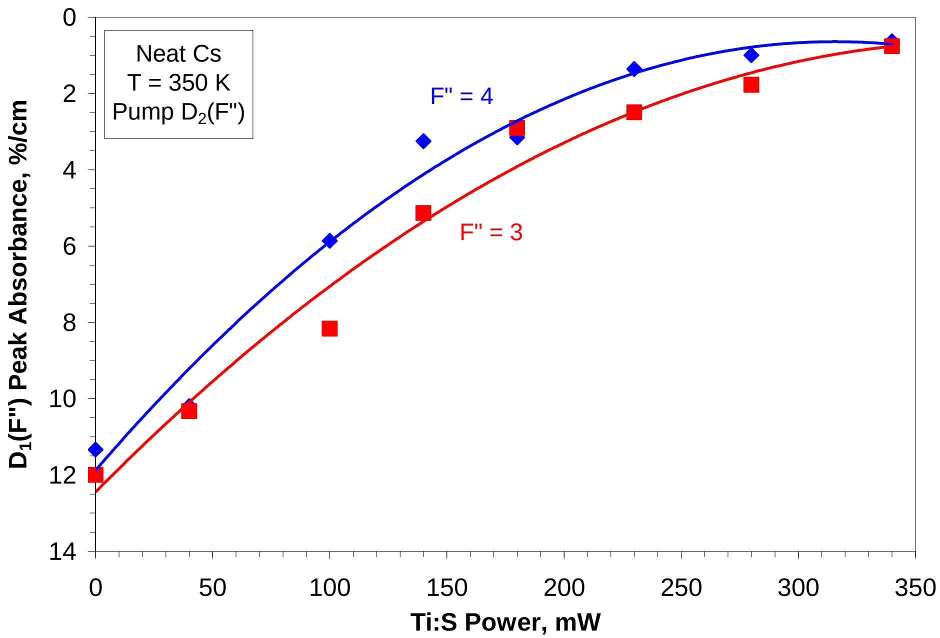
- **Continuing work: investigate absorption and gain dynamics for DPAL, XPAL configurations: Cs, Rb, K**

State-Selected Absorption and Saturation

Physical Sciences Inc.

VG10-174-24





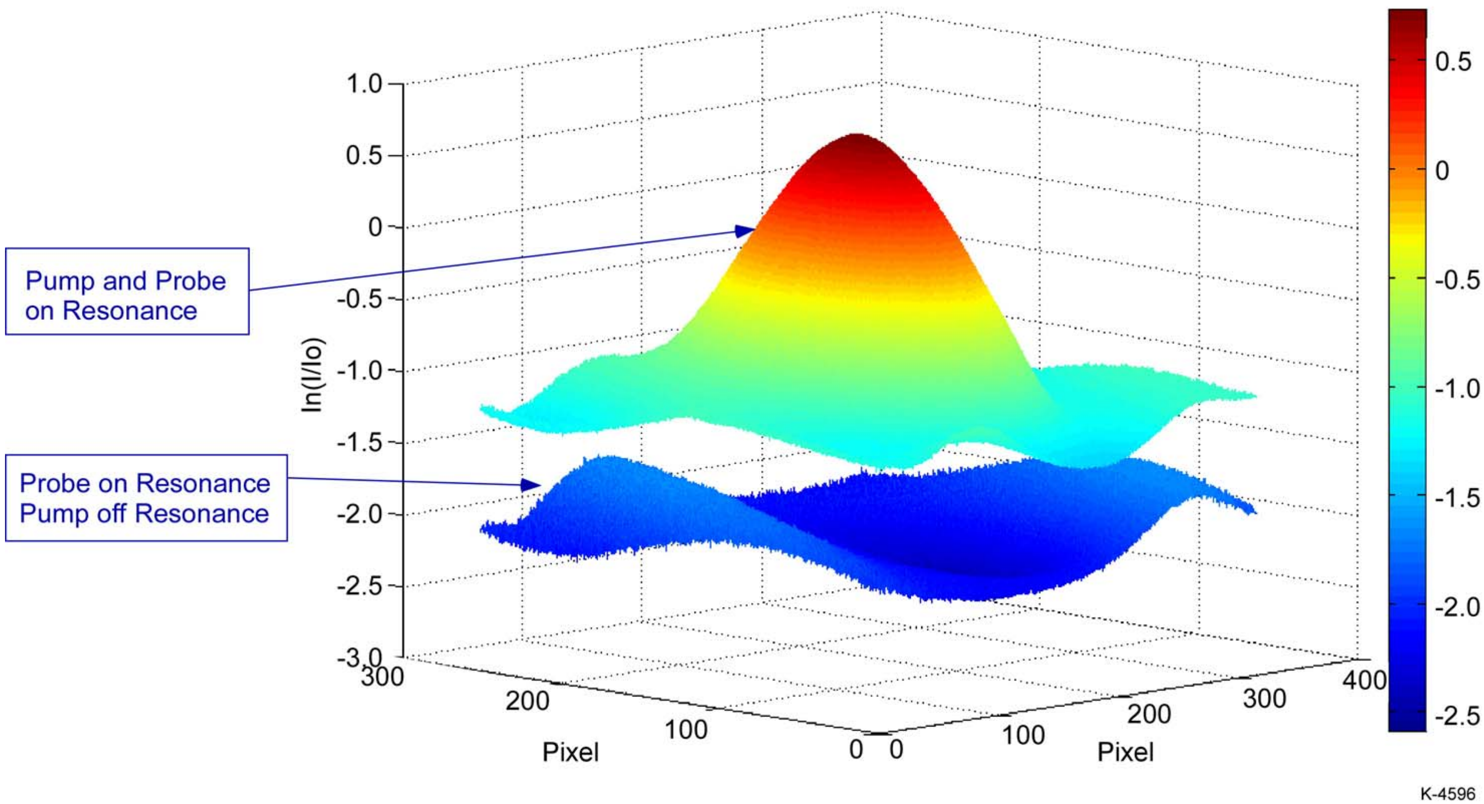
3-D Image of D_1 Gain, Absorption

Cs + 500 Torr Kr + 75 Torr C_2H_6

Physical Sciences Inc.

VG10-174-25

- **Probe beam diameter > pump beam diameter**
- **Sample 9 combinations: probe{on peak, off peak, blocked} x pump{on peak, off peak, blocked}**



- **Gain profile follows Gaussian profile of pump beam**

Conclusions

- **Multispecies diagnostic suite**
  - Absolute emission spectrometry
  - Ultrasensitive absorption photometry
  - Scanning TDL absorption/gain spectroscopy
- **Extreme sensitivity enables subscale operation at low species concentrations**
  - Simplify chemistry, focus on primary reaction steps
  - Transfer to large scale systems: establish models for scaling
- **EOIL, catalytic EOIL, COIL, micro-COIL: operational parametrics**
  - O_2(a) yield vs. small-signal gain
  - I_2 dissociation: [I_2], [I*] + [I]
  - O, O_3 effects
- **DPAL, XPAL: power scaling phenomena**
  - Gain vs. pump power, spatial effects at high optical depth
  - General emission spectroscopy: multi-photon effects vs. pump power

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