Detecting Localized Trace Species in Air Using Radar REMPI (Spin polarization and detection of Xe 129)

Richard B. Miles and Arthur Dogariu
Princeton University, Princeton, NJ 08540, USA
miles@princeton.edu

Remote Atmospheric Magnetometry Workshop
April 25 & 26, 2014

Mechanical and Aerospace Engineering
Applied Physics Group

Revolutionary Research . . . Relevant Results

Outline

- Radar REMPI (Resonantly Enhanced Multi-Photon Ionization)
- Trace detection (Nitric Oxide)
- Remote detection
- Xe spectra and detection
- Methods to spin polarize xenon
- Methods to detect spin polarized xenon

Trace species detection – Optical methods

- Absorption spectroscopy, Cavity-based techniques, Photo-Acoustic Spectroscopy, Polarization spectroscopy, Resonantly enhanced multi-photon ionization (REMPI), Mass spectrometry

- Rayleigh Scattering, Spontaneous Raman, Stimulated Raman, Coherent anti- Stokes Raman spectroscopy (CARS), Degenerate four-wave mixing (DFWM), Laser Induced Fluorescence (LIF), Light scattering (LIDAR)

- Laser Induced Breakdown Spectroscopy (LIBS)

Ideal true stand-off detection: no access to target (both source and detector), non-intrusive, localized if possible, high sensitivity and selectivity.

Possible Show Stoppers for Optical Detection

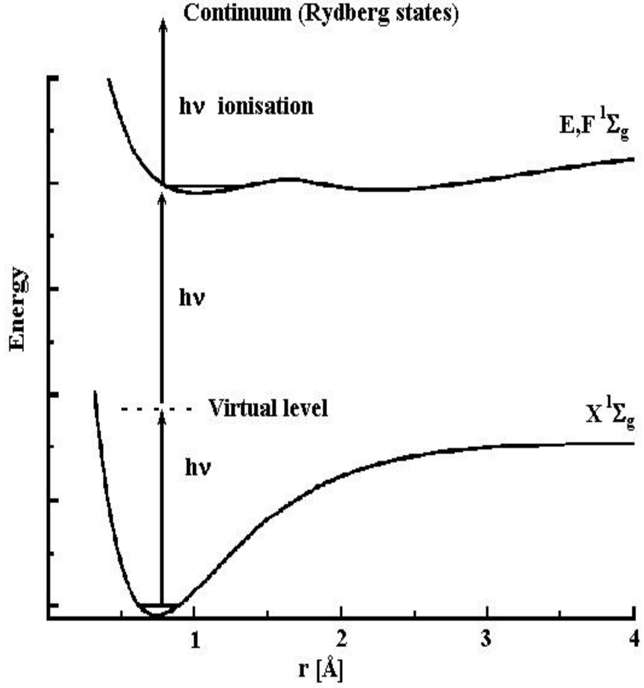
- Selectivity
  - Many molecules have similar spectral features. What is needed is a unique spectral feature in a transparent region of the atmosphere
  - Spectral features may be obscured by other air contaminants such as gasoline vapor
  - Spectral features may fall into a non atmospheric transparent region of the spectrum (<200nm in the vacuum UV)

- Detectivity
  - Photon limit – one photon (absorbed or emitted) per molecule is the maximum that is available for many approaches – usually much less due to the partition function
  - Most fluorescence lines are strongly quenched in the atmosphere
  - Incoherent signal – $1/r^2$ drop off in return signal
  - Shot noise
  - Laser induced fluorescence and other laser associated clutter
  - Solar Background

REMPI

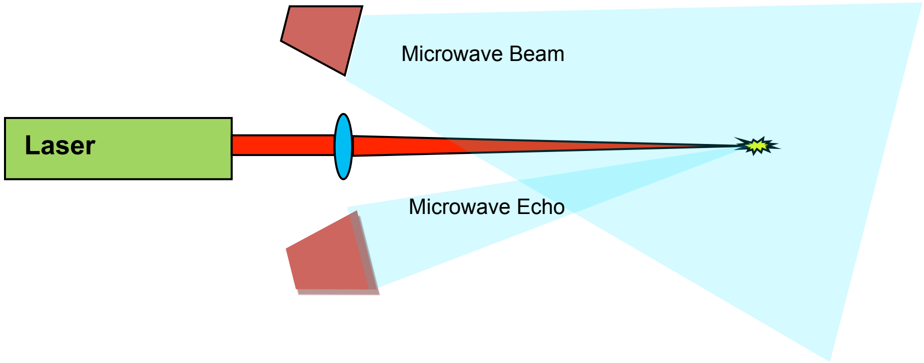
Resonantly Enhanced Multi-Photon Ionization:

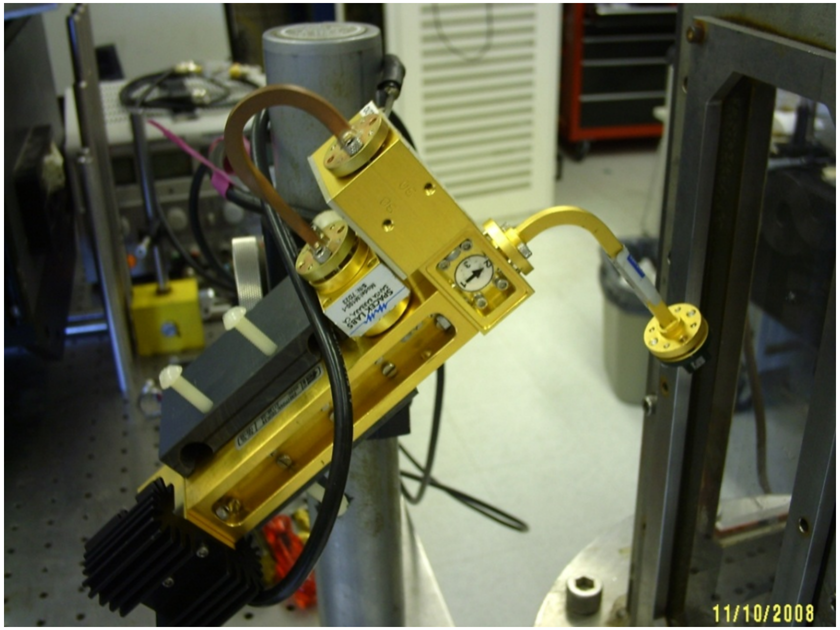
- An intense laser pulse ionizes the atom and creates charges/plasma.
  - The ionization is strongest when the photon(s) energy equals the energy difference between excited and ground state.
  - Extra photons bring the energy above the ionization energy of the atom (the energy required to remove one electron from an isolated, gas-phase atom).
  - Example: 2+1 REMPI = 2 photons to excite and 1 to ionize.
- Very high sensitivity and excellent selectivity
- Accesses spectral features that may be in non transparent regions of the surrounding gas
- Usually requires detection with electrodes or ion mass spectroscopy at low pressures.
- At atmospheric pressure, free electrons have a lifetime of ~10^{-8} sec due to attachment and recombination



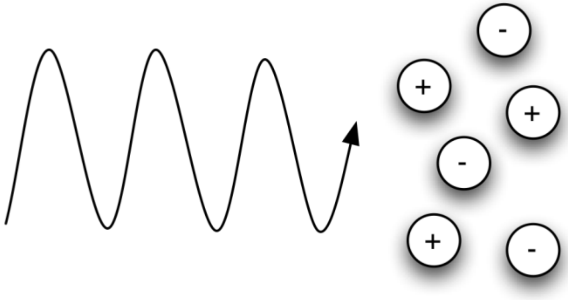
Radar REMPI

- Microwave scattering from laser-induced carriers.
- Microwave illuminates the ionization spot.
- Microwave scattering is collected.
- The interaction between plasma and microwave depends upon the skin depth of the plasma.



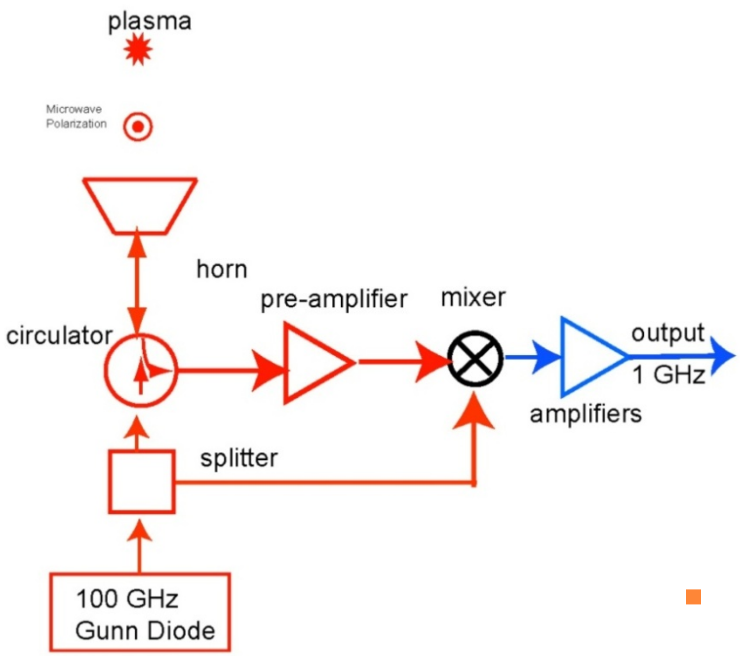


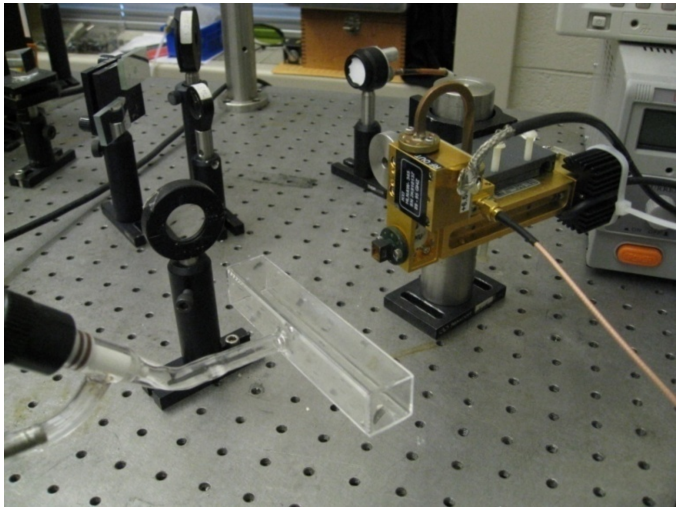
Microwave/laser measurement configuration. *The focused laser creates a small region of ionization and the microwaves are scattered from that region into the microwave detector.*



$$\delta = \delta(\sigma, \omega)$$

Radar REMPI: Microwave Detection



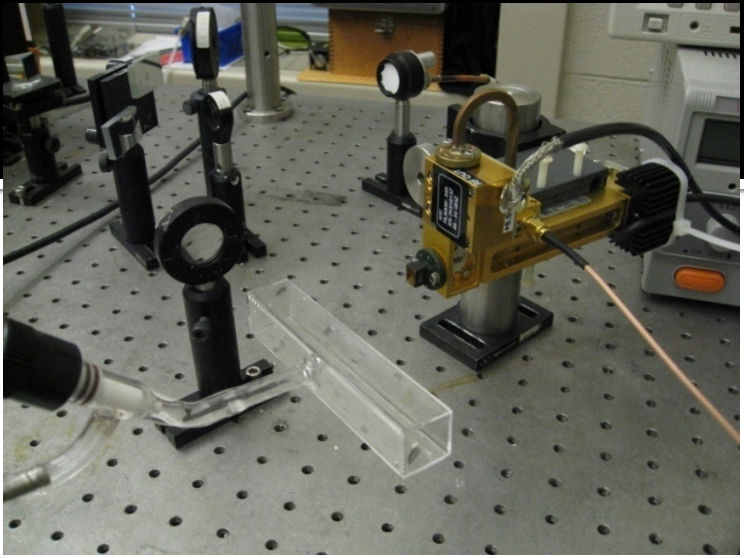


- Homodyne 100 GHz system.
- 100 GHz probes the plasma.
- The mixer output is proportional with the scattering amplitude, hence electron density

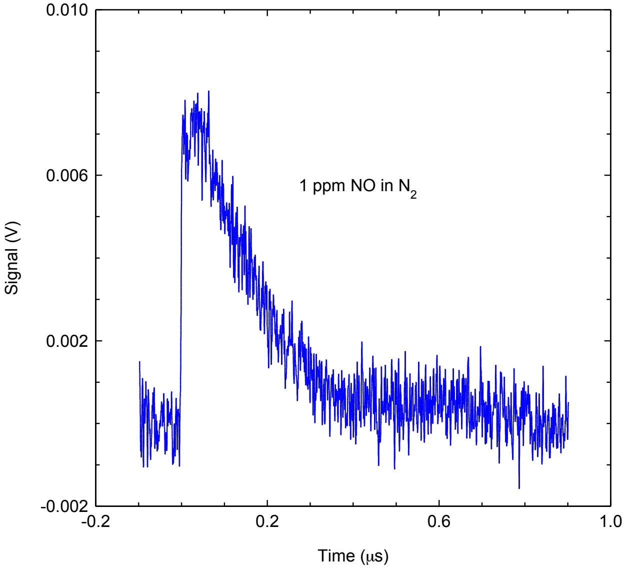
- Selectivity and sensitivity: independent!
  - Selectivity: laser wavelength ($\Delta\lambda \approx$ cm^{-1})
  - Sensitivity : microwave detection
- Truly standoff – backscattering detection
- Non-intrusive, localized (laser spot)
- No daylight optical interference
- Bonus: sub-nanosecond temporal resolution!

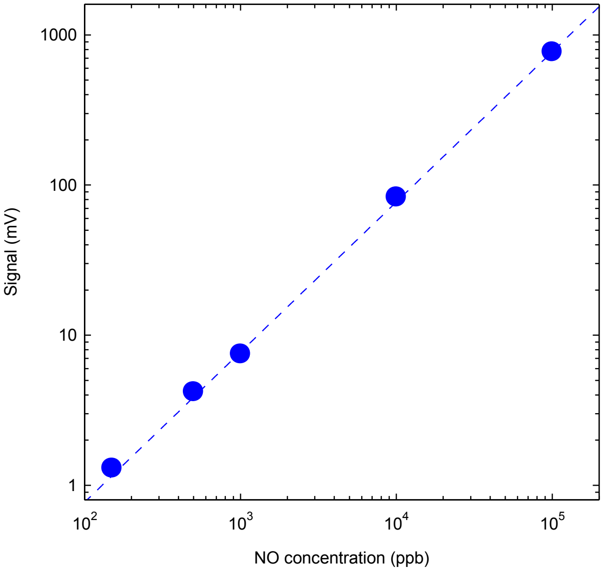
Nitric Oxide Detection

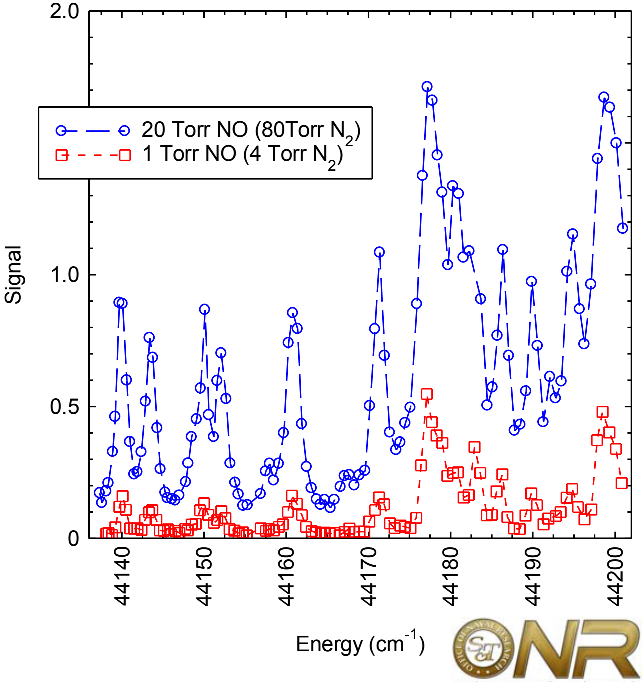
- Linearity from ppm to ppb
- High temporal resolution
- Detection sensitivity – ppb



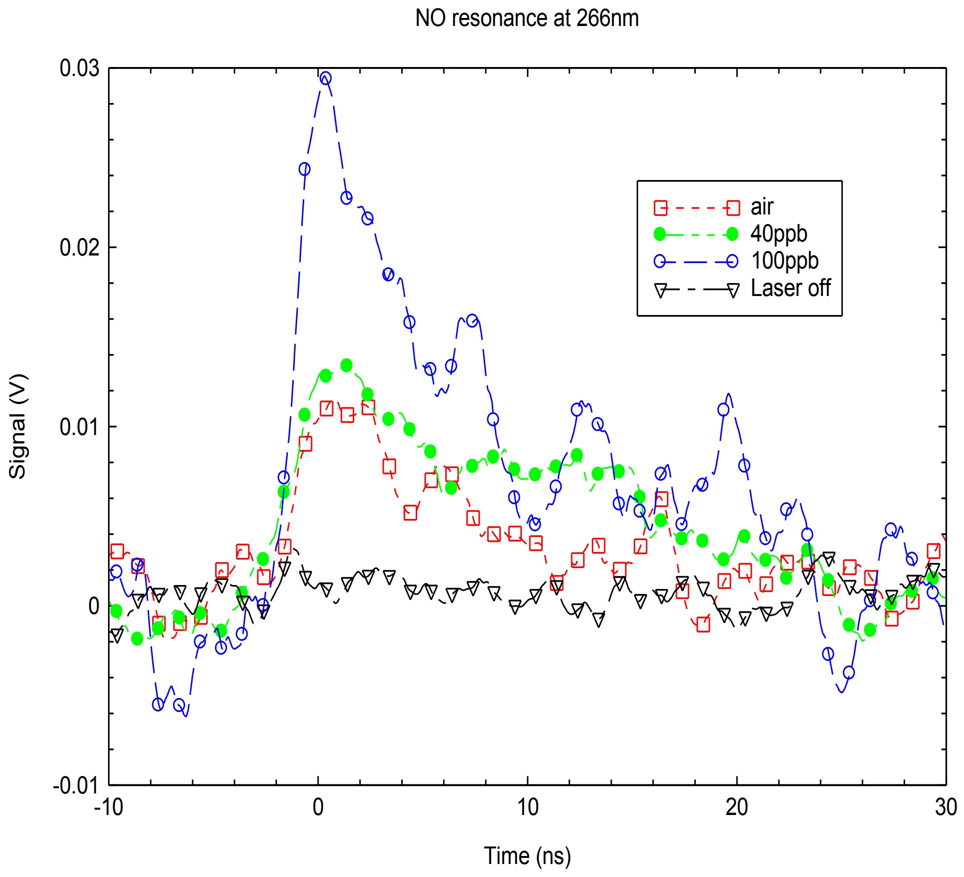
A. Dogariu and R. B. Miles, *Appl. Opt.* **50,** A68 (2011).






1+1 Radar REMPI in NO

Detection sensitivity for Nitric Oxide in atmospheric air



- We reduce NO to ppb!
- Signal for 10 and 40ppb, same as air
- Level of NO in air: ~40 ppb
- Literature: 0.4-100 ppb

- Detection of NO in air with ppb accuracy.

- Ppb levels: record for true stand-off detection of trace species.
- Backscattered (not “through”) detection, no background light interference

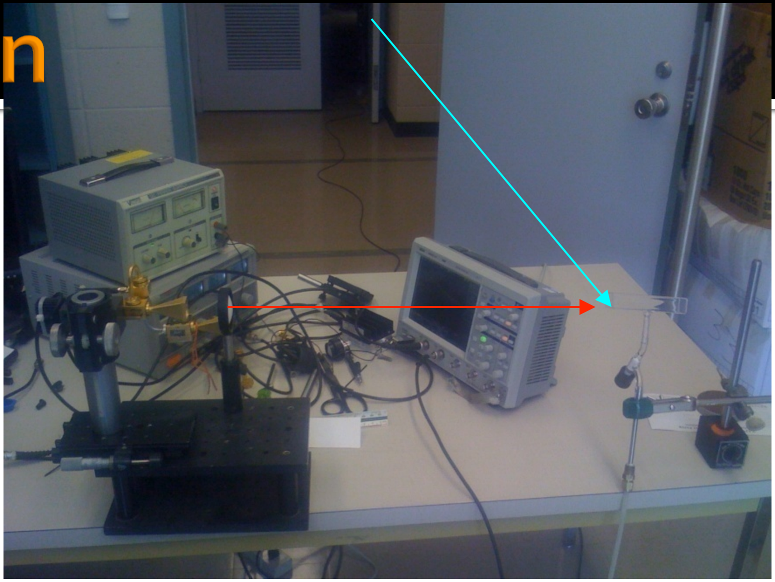
A. Dogariu and R. B. Miles, *Appl. Opt.* **50,** A68 (2011).

Princeton University

ONR Revolutionary Research . . . Relevant Results

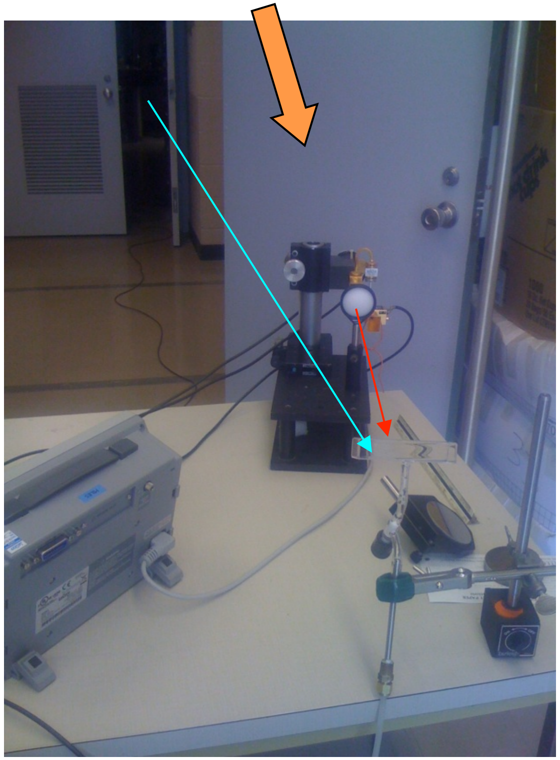
Weakly ionized Plasma: Rayleigh Scattering Standoff NO detection

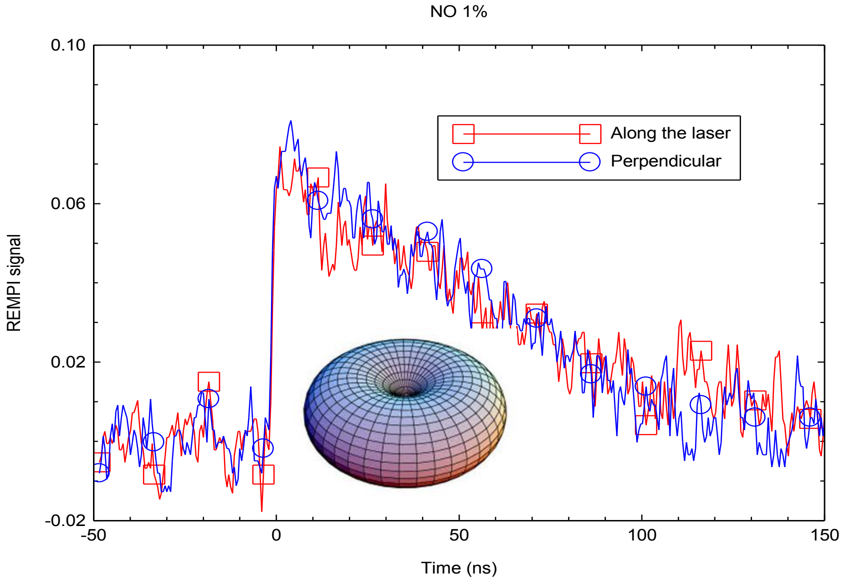
Detection:
Perpendicular to the laser



Along the laser

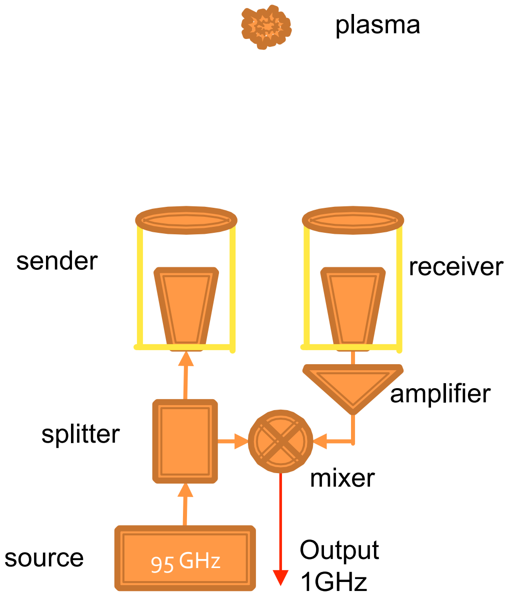
226 nm laser
is 10 m away

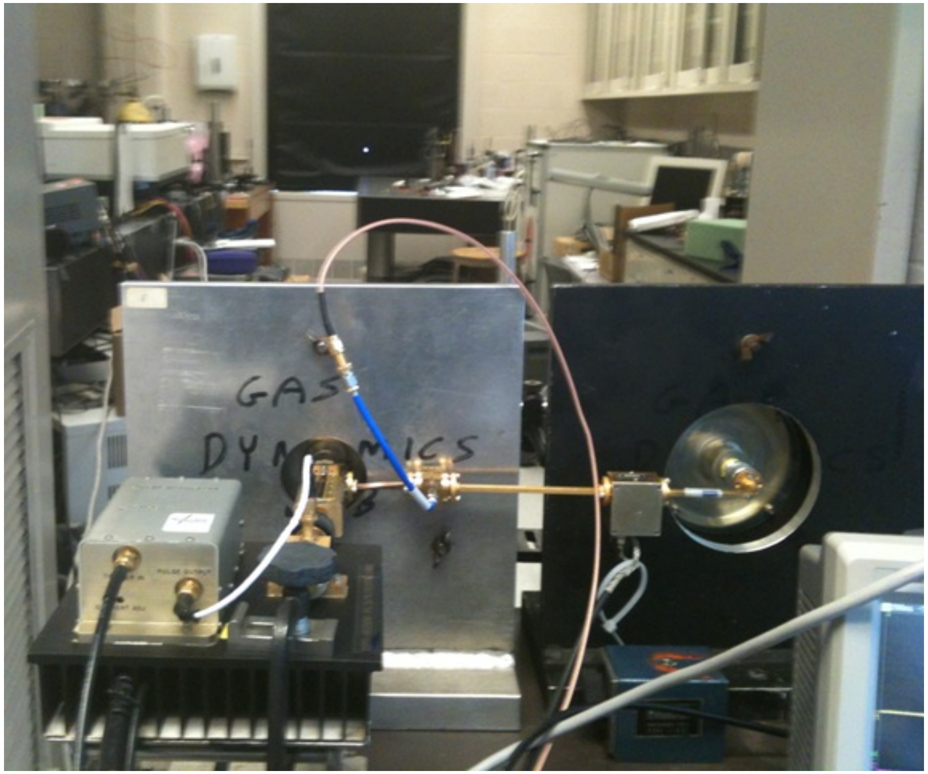




Suitable for standoff detection!

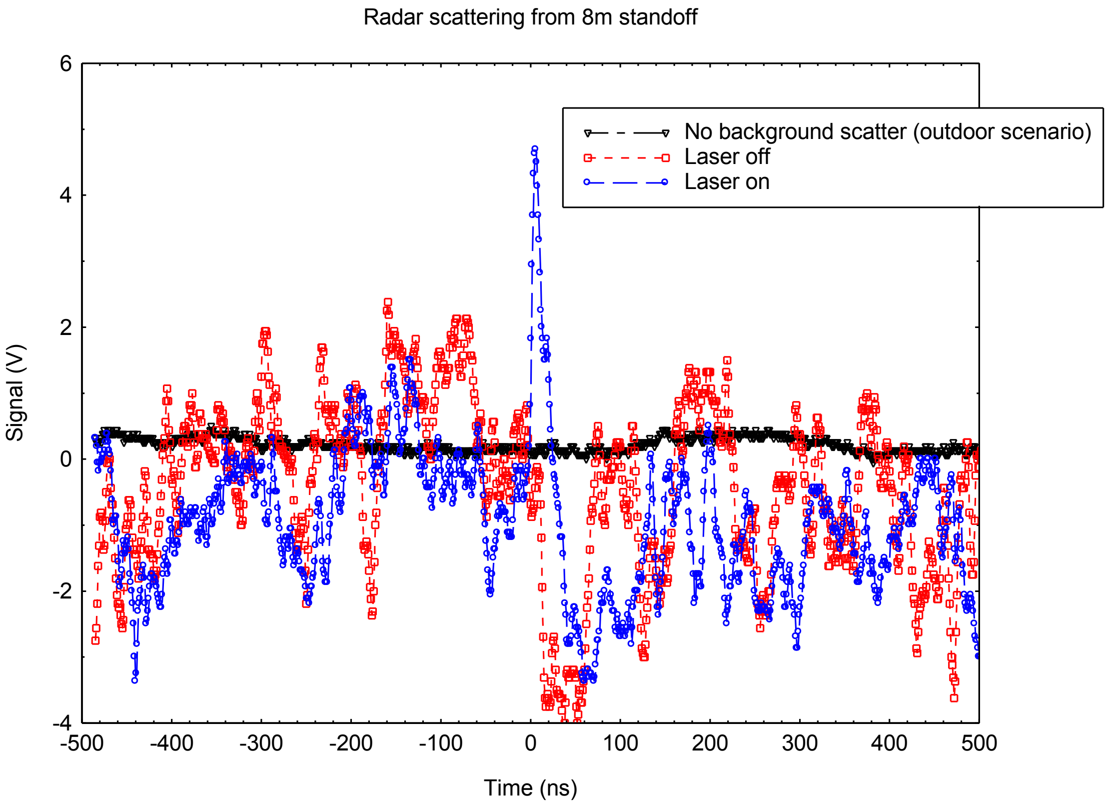
Standoff Radar detection



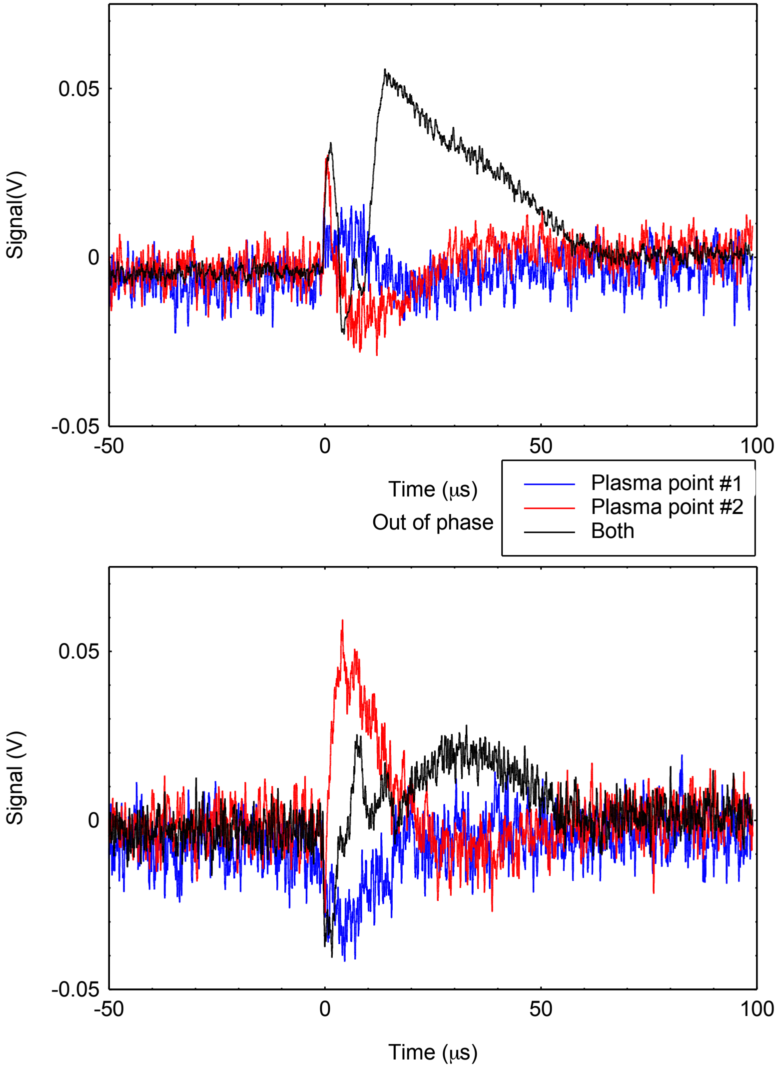


- 95 GHz microwave system
  400mW source
- Laser induced plasma –
  25 ft. away
- 1-10 microsecond pulses (or CW)
- Dual lens system (sender/receiver)
- Phase sensitive homodyne detection

25ft standoff distance



Coherent signal enhancement



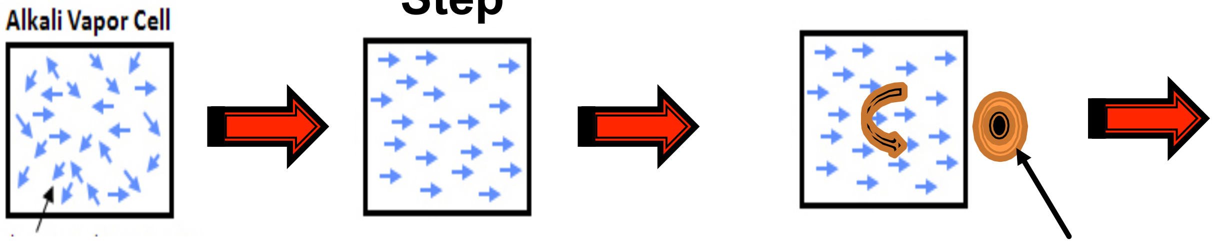
- Two laser induced plasma spots
- Standoff distance: 25 feet
- Moving one spot by 1.5mm ($\lambda/2$) changes the signal (electric field) by $\pi/2$ (blue curve)
- Signal from both adds constructively (in phase) or destructively (out of phase)
- Bragg scattering enhances the signal in the backscattered direction.

Approaches to Improve Detectivity

- Increased microwave power and intensity
  - Pulse the microwave synchronously with the laser
  - Focus the microwaves to increase the intensity
- Increase the microwave detection bandwidth
  - Use sharp leading edge of the time response
  - Differential detection (before and after the leading edge)
- Use coherent array of laser spots to enhance backscattering
- Use heterodyne detection with phase sensitivity
- Use microwave detector array
- Use coherent addition from sequential pulses (synthetic aperture radar)
- Optimize the microwave frequency

Atomic Magnetometry

- **Magnetometry**: Measurement of the strength of a magnetic field
  - Here, we restrict this discussion to scalar magnetometry
- **Atomic magnetometry:** "*Device that makes use of resonant light to create long lived orientations, which undergo larmor precession in a magnetic field. This precession can then be measured in terms of a change in the optical absorptive or dispersive properties of these atoms.*" – Budker and Romalis (2007)



Preparation Step

Randomly oriented spins

Optical pumping to hyperpolarize the atoms

In the presence of a B field, these atoms precess

Detection & measurement of this precession, ω_L

Remote Magnetometry

- Hyperpolarization (spin polarization) has to be effected remotely
- Choice of spin polarized gas has to be naturally occurring in the earth's atmosphere
  - Preferably in (relatively) large amounts
- Concentrations of this gas should be fairly constant within regions where magnetic field measurements are expected to be made
  - Noble gases are ideal since they are inert

Choice of Spin Polarized C

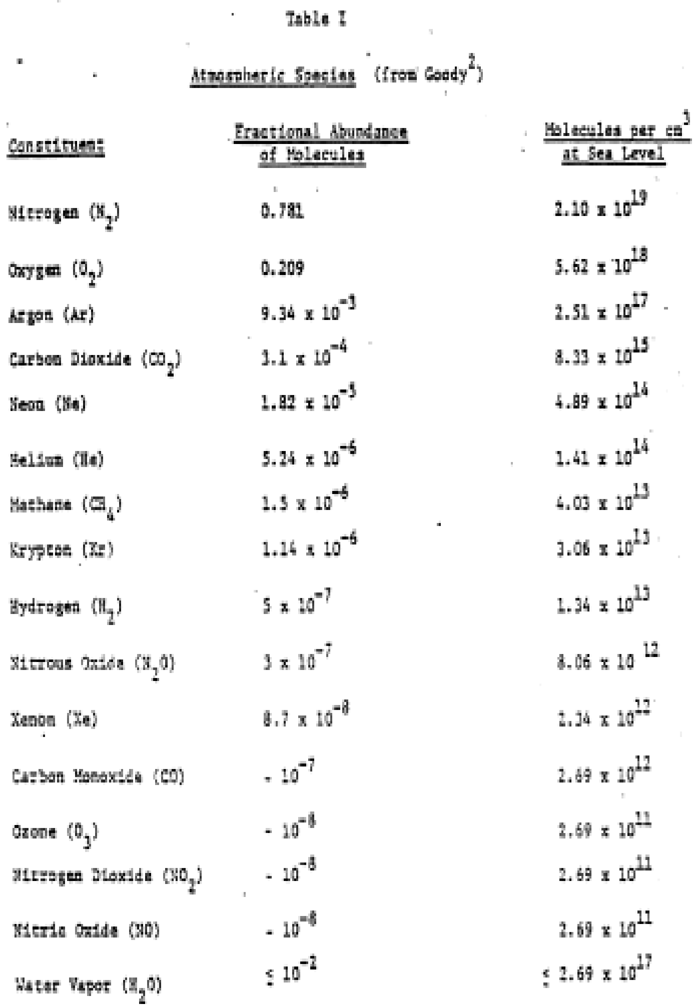


Table I

Atmospheric Species (from Goody[2])

Constituent	Fractional Abundance of Molecules	Molecules per cm^3 at Sea Level
Nitrogen (N_2)	0.781	2.10×10^{19}
Oxygen (O_2)	0.209	5.62×10^{18}
Argon (Ar)	9.34×10^{-3}	2.51×10^{17}
Carbon Dioxide (CO_2)	3.1×10^{-4}	8.33×10^{15}
Neon (Ne)	1.82×10^{-5}	4.89×10^{14}
Helium (He)	5.24×10^{-6}	1.41×10^{14}
Methane (CH_4)	1.5×10^{-6}	4.03×10^{13}
Krypton (Kr)	1.14×10^{-6}	3.06×10^{13}
Hydrogen (H_2)	5×10^{-7}	1.34×10^{13}
Nitrous Oxide (N_2O)	3×10^{-7}	8.06×10^{12}
Xenon (Xe)	8.7×10^{-8}	2.34×10^{12}
Carbon Monoxide (CO)	$\sim 10^{-7}$	2.69×10^{12}
Ozone (O_3)	$\sim 10^{-8}$	2.69×10^{11}
Nitrogen Dioxide (NO_2)	$\sim 10^{-8}$	2.69×10^{11}
Nitric Oxide (NO)	$\sim 10^{-8}$	2.69×10^{11}
Water Vapor (H_2O)	$\leq 10^{-2}$	$\leq 2.69 \times 10^{17}$

Criteria

- Inert
- Non-zero nuclear spin
- Large gyromagnetic ratio,
- Nuclear magnetic linewidths of **diatomics or polyatomics** usually > **monatomics**

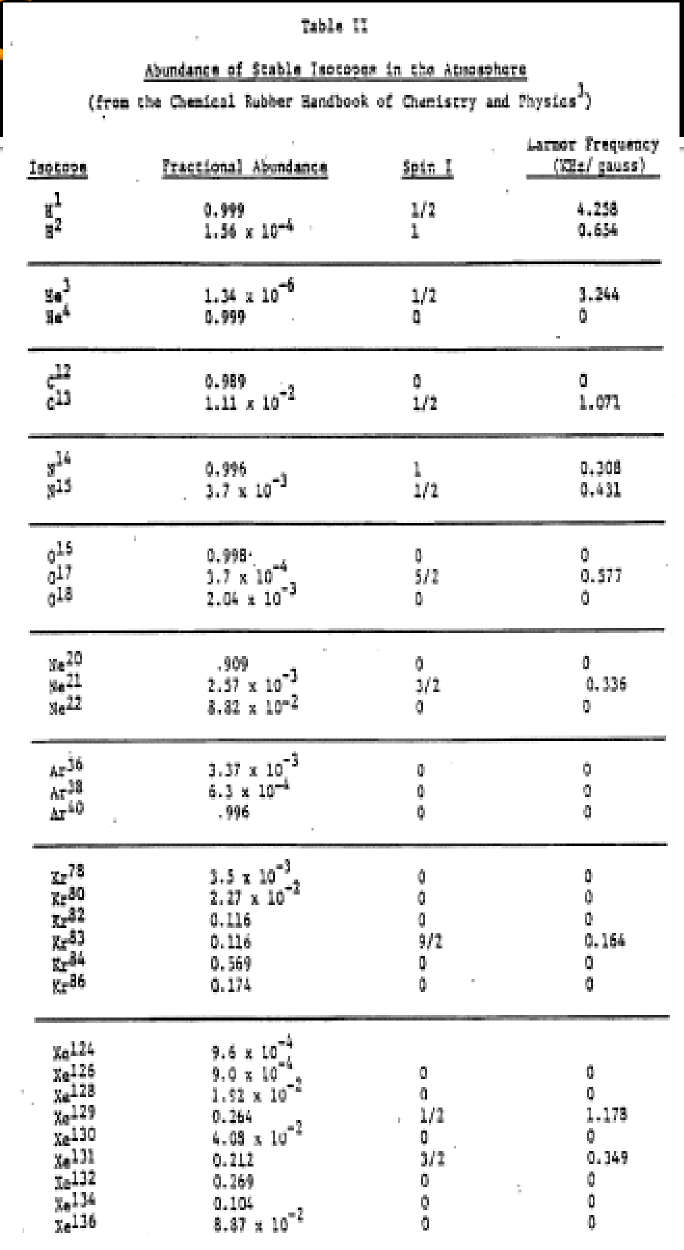


Table II

Abundance of Stable Isotopes in the Atmosphere

(from the Chemical Rubber Handbook of Chemistry and Physics[3])

Isotope	Fractional Abundance	Spin I	Larmor Frequency (KHz/ gauss)
H^1	0.999	1/2	4.258
H^2	1.56×10^{-4}	1	0.654
He^3	1.34×10^{-6}	1/2	3.244
He^4	0.999	0	0
C^{12}	0.989	0	0
C^{13}	1.11×10^{-2}	1/2	1.071
N^{14}	0.996	1	0.308
N^{15}	3.7×10^{-3}	1/2	0.431
O^{15}	0.998	0	0
O^{17}	3.7×10^{-4}	5/2	0.577
O^{18}	2.04×10^{-3}	0	0
Ne^{20}	.909	0	0
Ne^{21}	2.57×10^{-3}	3/2	0.336
Ne^{22}	8.82×10^{-2}	0	0
Ar^{36}	3.37×10^{-3}	0	0
Ar^{38}	6.3×10^{-4}	0	0
Ar^{40}	.996	0	0
Kr^{78}	3.5×10^{-3}	0	0
Kr^{80}	2.27×10^{-2}	0	0
Kr^{82}	0.116	0	0
Kr^{83}	0.116	9/2	0.164
Kr^{84}	0.569	0	0
Kr^{86}	0.174	0	0
Xe^{124}	9.6×10^{-4}		
Xe^{126}	9.0×10^{-4}	0	0
Xe^{128}	1.92×10^{-2}	0	0
Xe^{129}	0.264	1/2	1.178
Xe^{130}	4.08×10^{-2}	0	0
Xe^{131}	0.212	3/2	0.349
Xe^{132}	0.269	0	0
Xe^{134}	0.104	0	0
Xe^{136}	8.87×10^{-2}	0	0

Happer, 1989

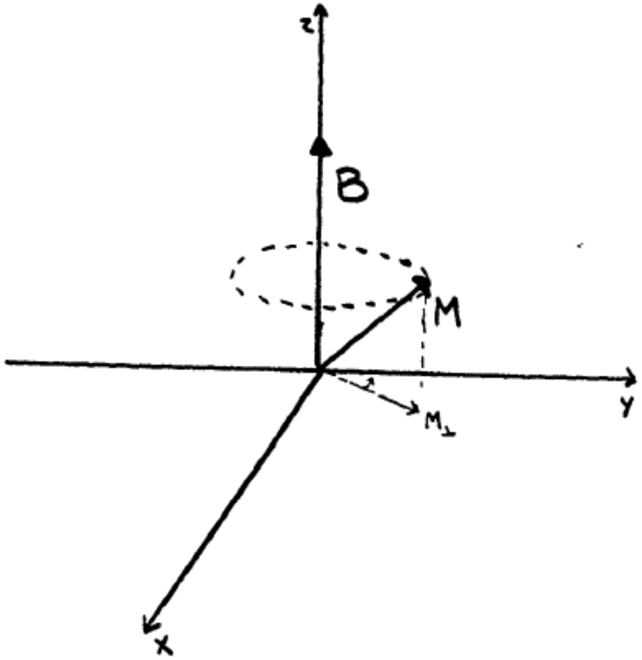
Xe^{129} as a magnetic sensor

- Present in atmospheric air: 26% of total Xe, or $6x10^{11}cm^{-3}$
- Chemically inert, not affected by local conditions
- Nuclear spin = 1/2
- Nuclear magnetic relaxation time – seconds
- Multi-photon optical pumping possible

Happer, W., "Laser Remote Sensing of Magnetic Fields in the Atmosphere by Two-Photon Optical Pumping of Xe^{129}" NADC Report N62269-78-M-6957 (1978)

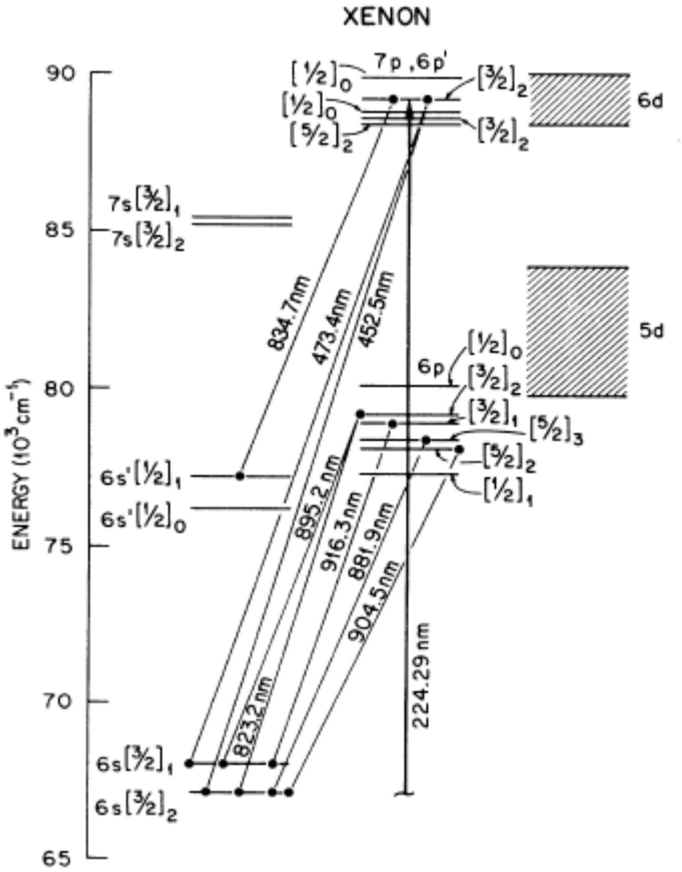
Xe^{129} as a magnetic sensor

- Atoms in one of the two spin states (nuclear magnetic moment M) will precess in the earth's magnetic field (B) at 1.178kHz/gauss (Larmor frequency)

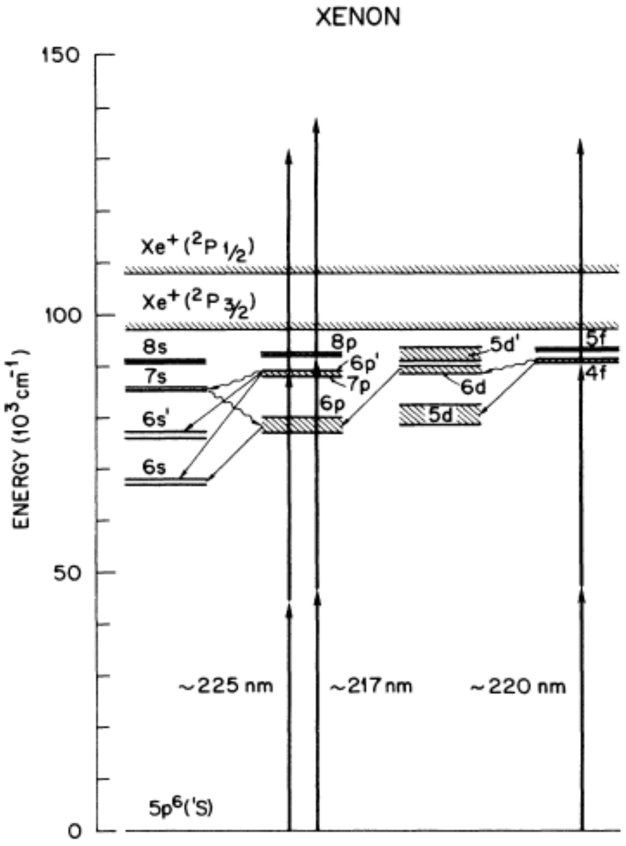


Martin Squicciarini, "The Feasibility of Detecting a Magnetic Field From a Distant Platform," Naval Air Development Center Report, May 15, 1987

Energy Levels and Transitions in Xenon

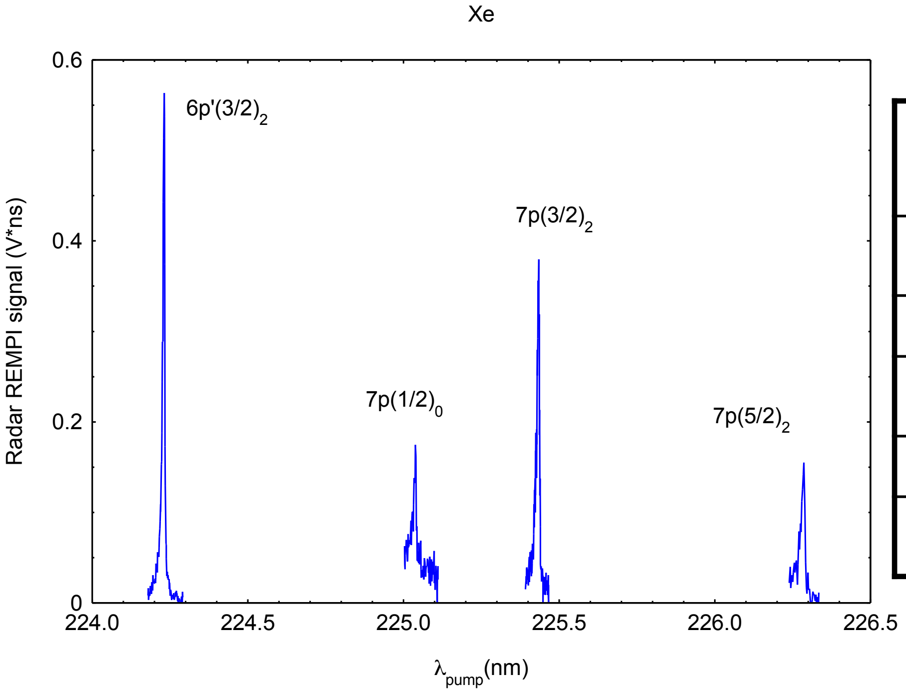


Two-Photon Absorption LIF



Radar REMPI

2+1 Radar REMPI spectra of Xe: allowed two-photon transitions

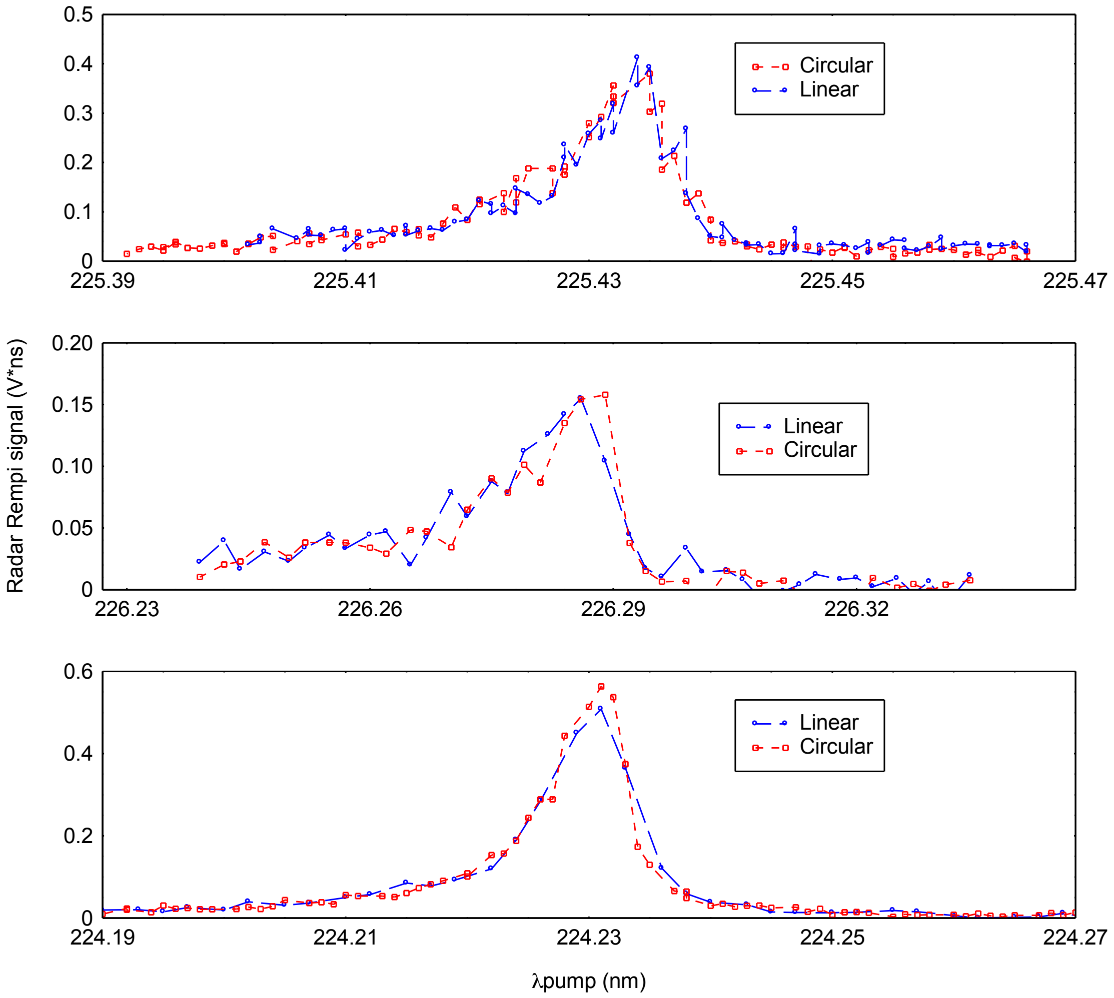


Excited State ($5p^5$)	ΔJ	Energy (cm^{-1})	$\lambda_{2\text{-photon}}$ (nm)	Linear (ΔJ= 0,±1, ±2)	Circular (ΔJ=±2)
7p(5/2)$_2$	+2	88,351.681	226.3	Yes	Yes
7p(3/2)$_2$	+2	88,686.500	225.4	Yes	Yes
7p(1/2)$_0$	0	88,842.256	225.1	Yes	No
6p’(3/2)$_2$	+2	89,162.356	224.3	Yes	Yes
6p’(1/2)$_0$	0	89,860.015	222.6	Yes	No

Ground state: $5p^6\ {}^1S_0$

Two-photon excitation spectrum of Xe obtained via 2+1 Radar REMPI

Same signals for linear and circular polarization for J=2 states

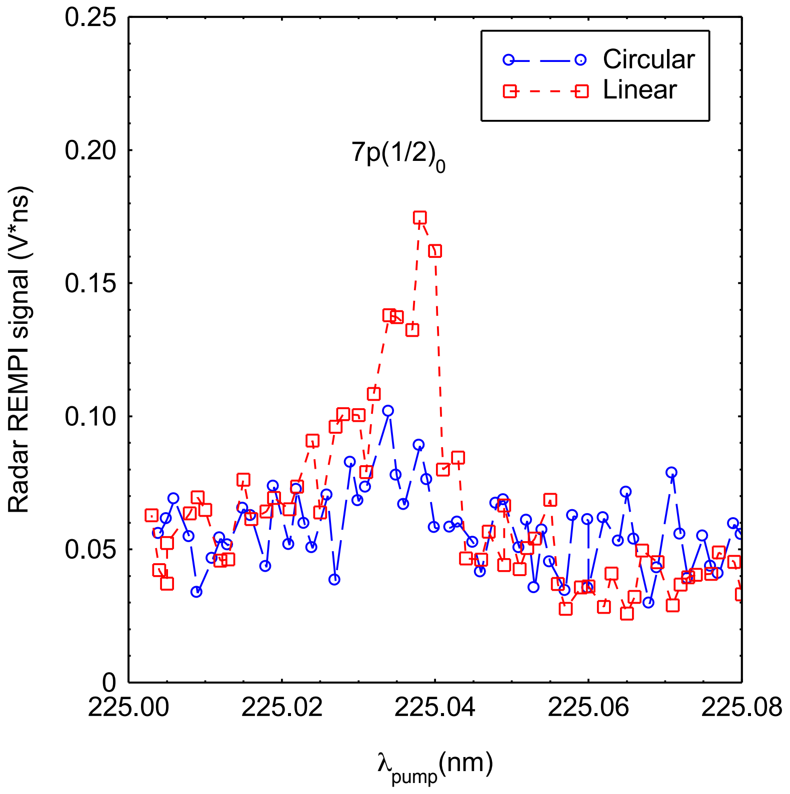


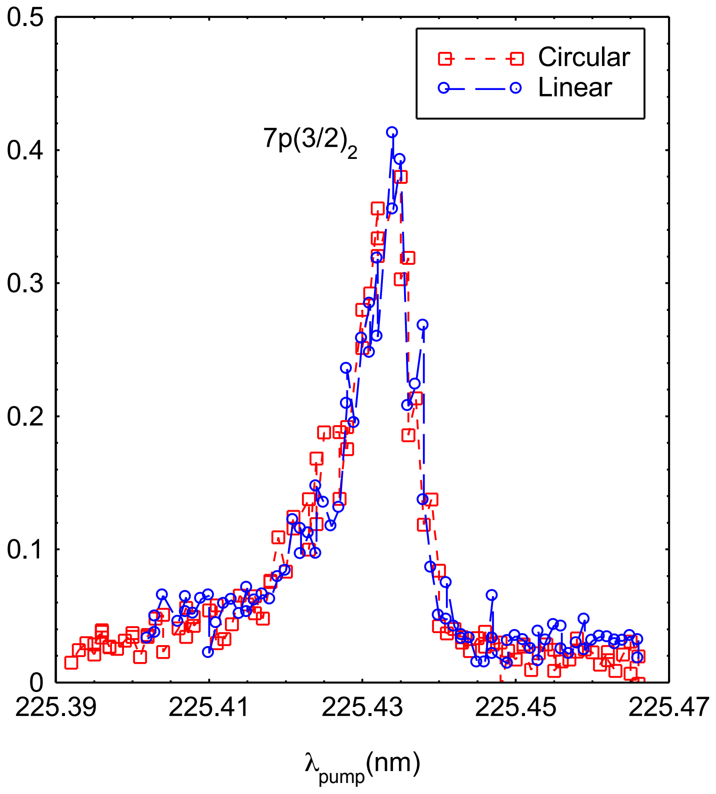
$\Delta J = +2$ $7p(3/2)_2$

$\Delta J = +2$ $7p(5/2)_2$

$\Delta J = +2$ $6p'(3/2)_2$

Circular vs. Linear Polarization

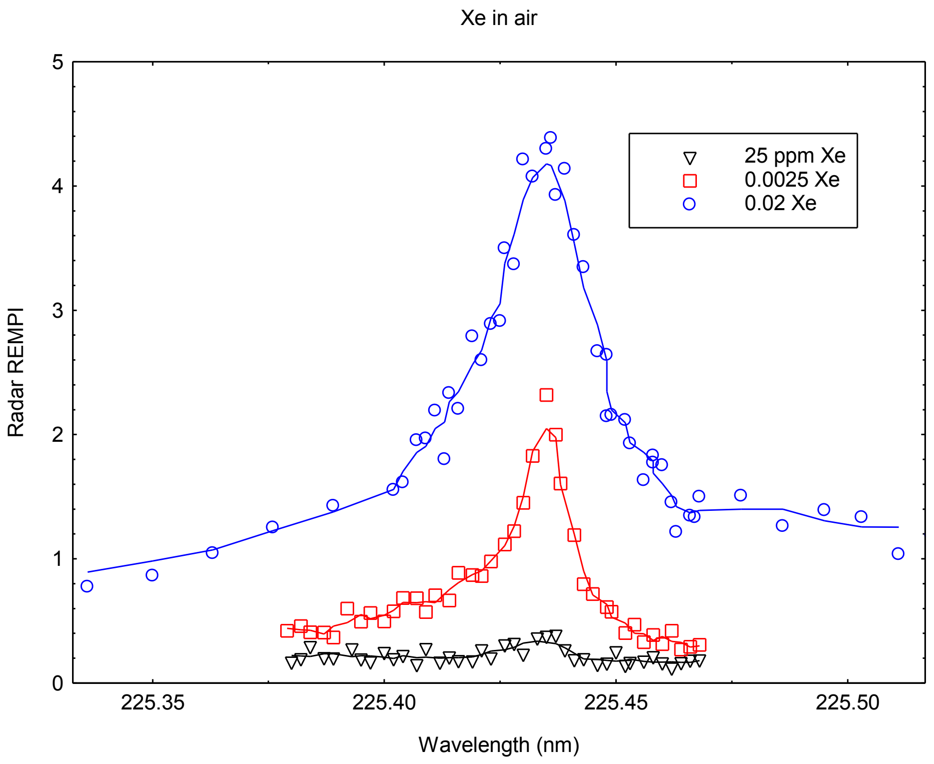


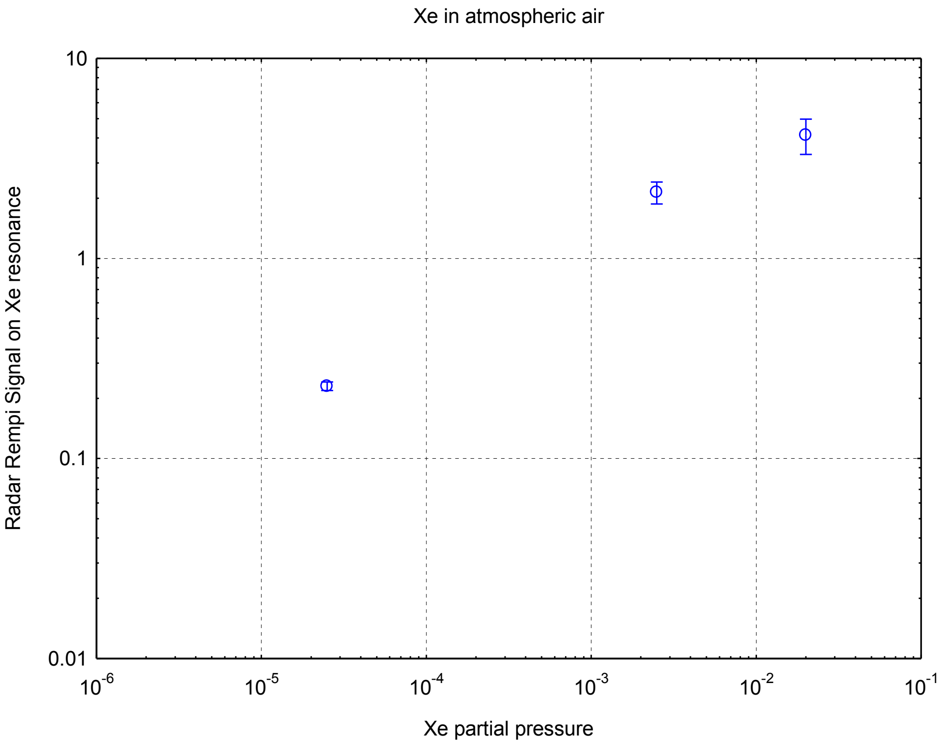


$\Delta J = 0$ $7p(1/2)_0$

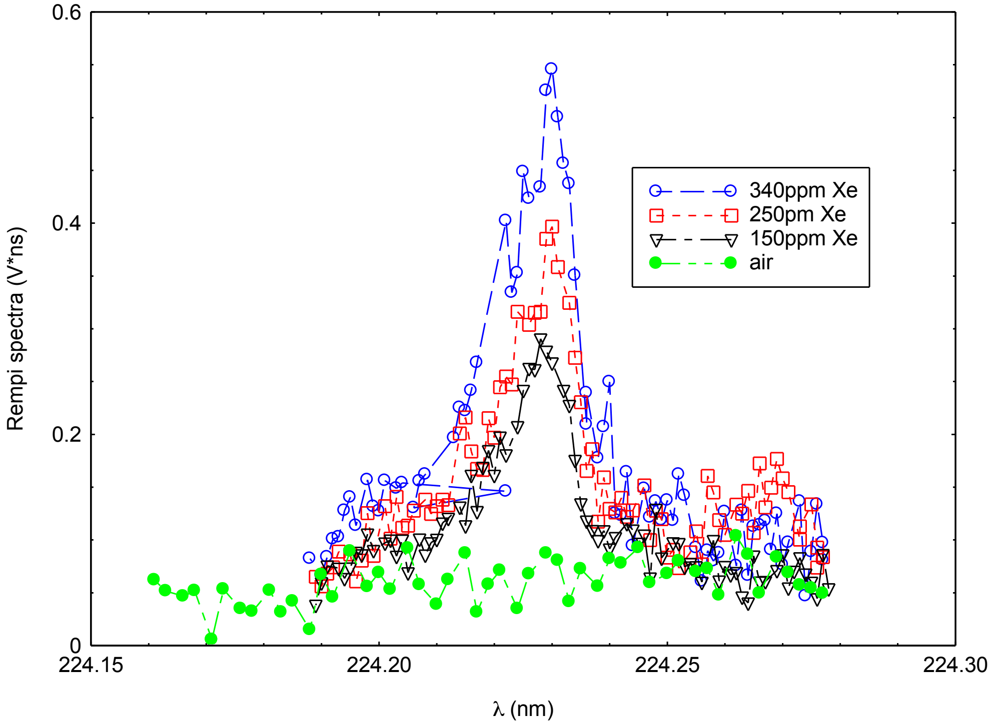
$\Delta J = +2$ $7p(3/2)_2$

Radar REMPI Detection of Xenon trace in air





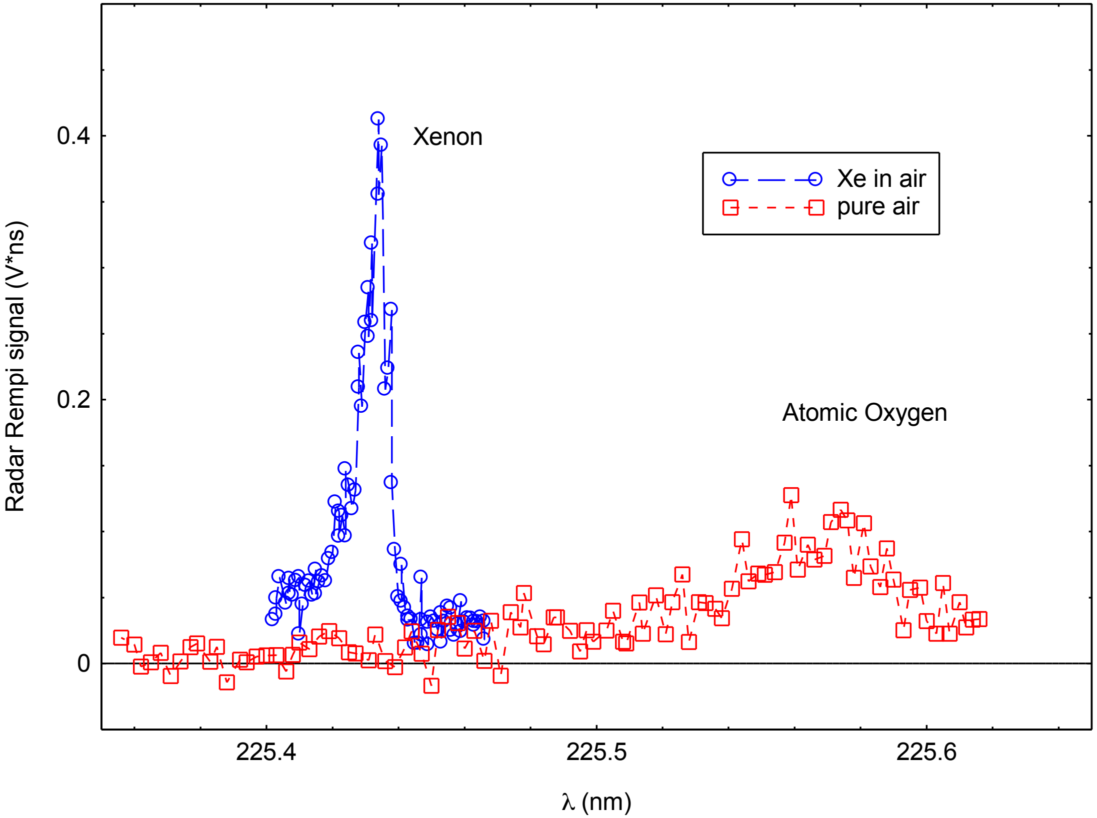
Xe spectra in air



Spectra of the 6p'$(3/2)_2$ line for Xe in air.

Interferents in detecting atmospheric Xe

The 226nm pump laser dissociates oxygen molecules, creating atomic oxygen.



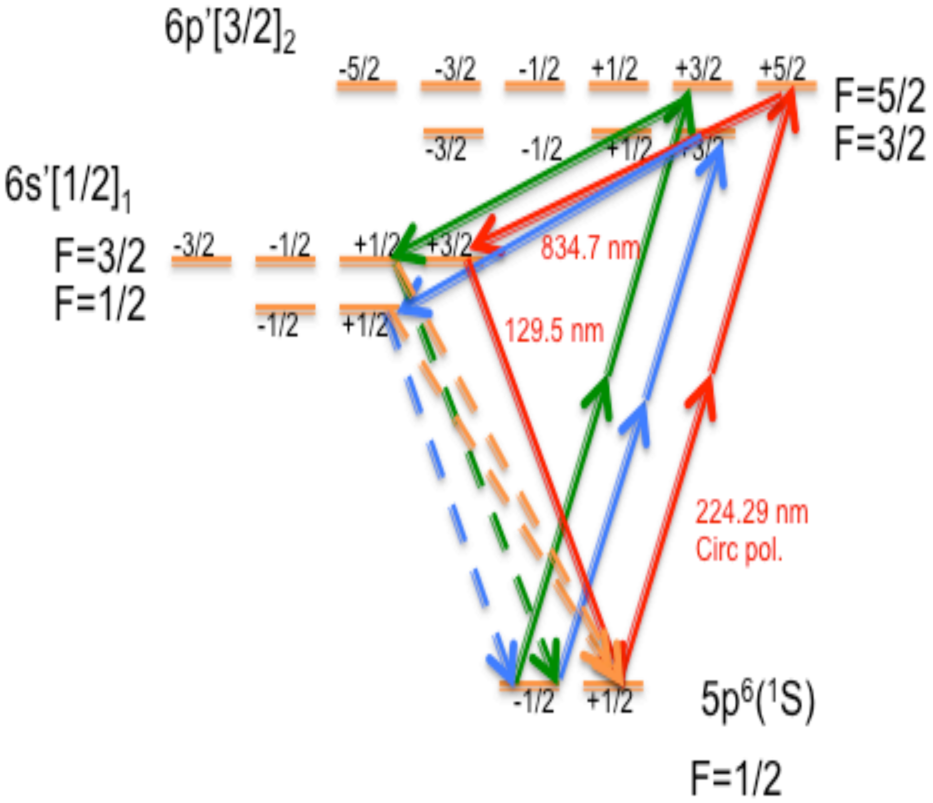
The $7p(3/2)_2$ Xe line vs. photolytic atomic oxygen

Princeton University

Xe 129 Pumping Concepts

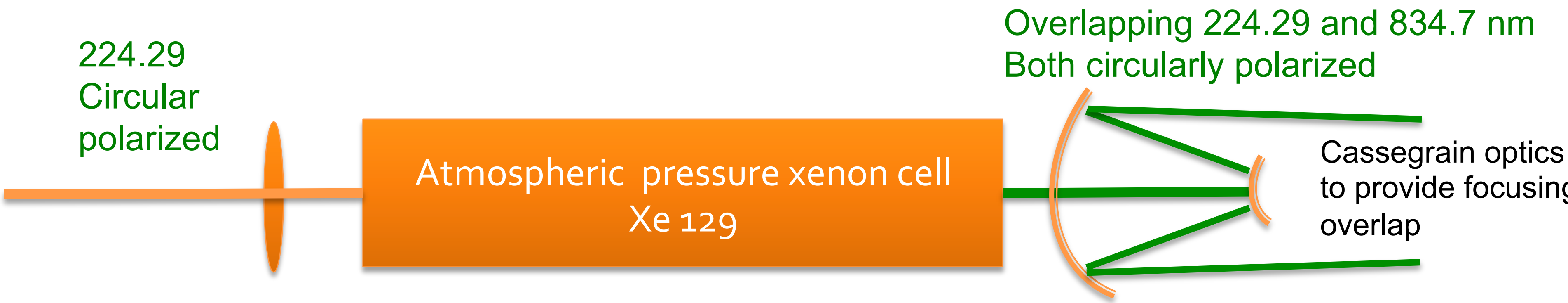
- Double resonant three photon pumping
  - Circular polarized 224.29 nm
  - Circular polarized 834.7nm
    - Generated by passing 224.29 nm light through a xenon cell using resonant driven lasing process similar to air laser in N and O.
    - Both beams focused with reflecting optics
- Single photon resonant pumping with locally generated, circularly polarized 129 nm light
  - Uses resonant and non resonant four wave mixing in air
  - Quasi phase matched in the forward direction
  - 129 nm has ~4mm absorption length in air << coherence length

Remote Preparation of Spin Polarized ^{129}Xe by collinear double resonant nonlinear pumping



- Two co-propagating beams at 224.3 nm and 834.7 nm
- By virtue of the selection rules:
  - Atoms pumped from the m= +1/2 ground state (red loop) are trapped in that loop, i.e. eventually end up back in the m=+1/2 ground state
  - Atoms pumped from the m=-1/2 ground state (green & blue loops) have a chance of ending up in either of the ground states
  - Net effect is an eventual population of the m=+1/2 ground state

Generating the four wave mixing pump laser



224.29
Circular
polarized

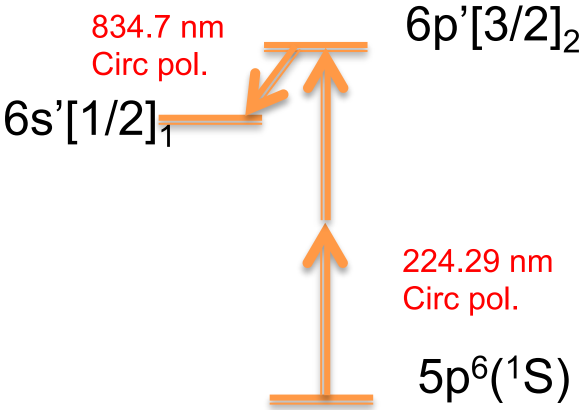
Atmospheric pressure xenon cell
Xe 129

Overlapping 224.29 and 834.7 nm
Both circularly polarized

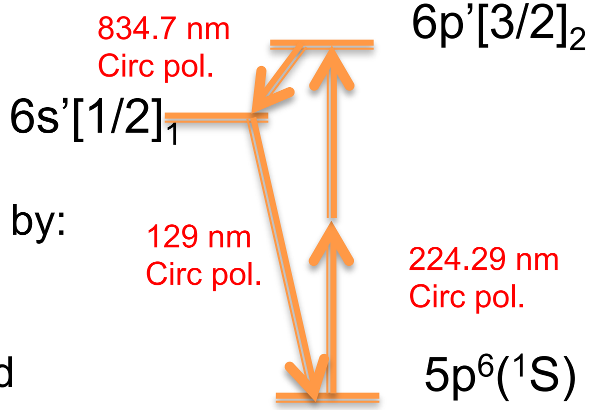
Cassegrain optics
to provide focusin
overlap

Stimulated emission generated at 834.7

Similar process as the oxygen and nitrogen air lasers, but no dissociation needed.

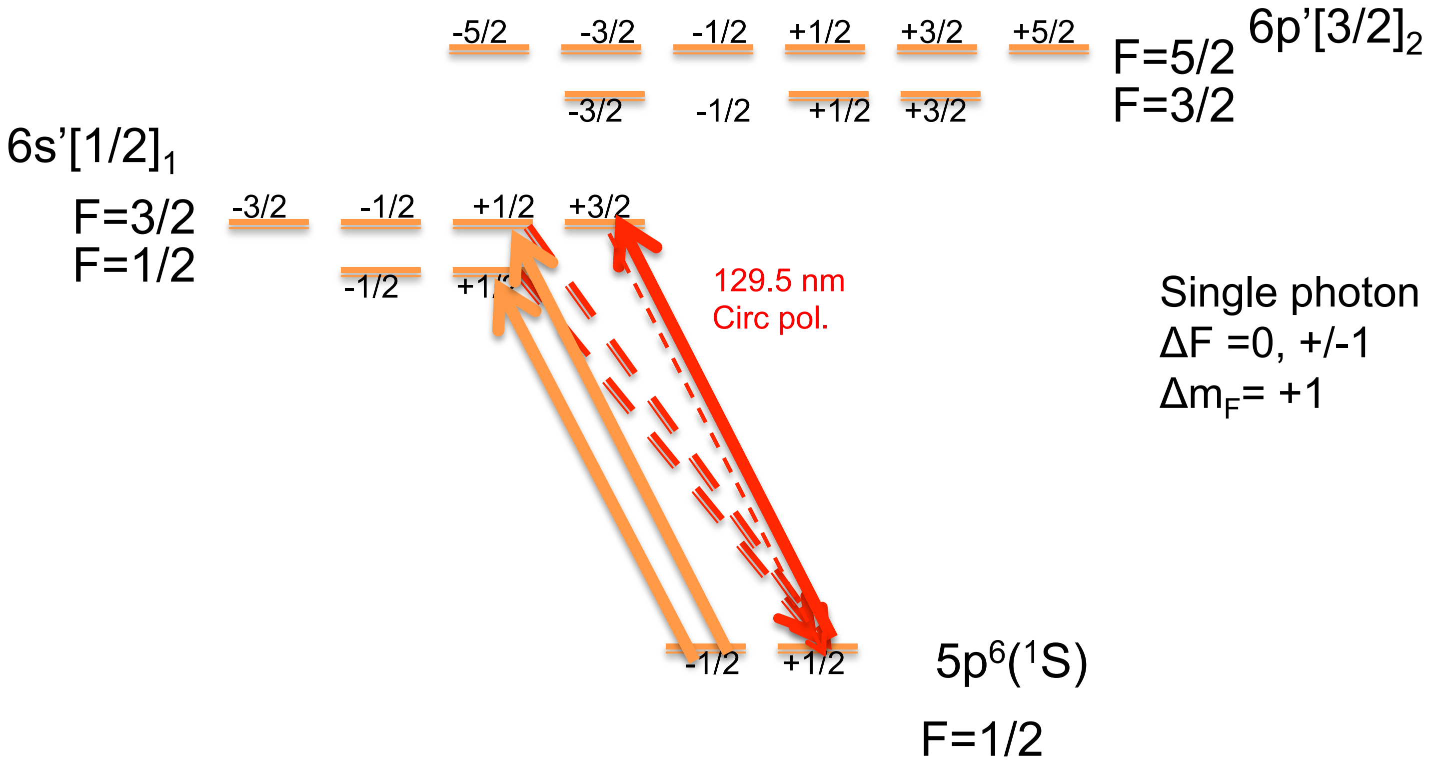


Followed by:
Collinear resonant enhanced four wave mixing



Princeton University

Optical pumping to m_F=+1/2 ground state by direct absorption of 129 nm circular polarized light.



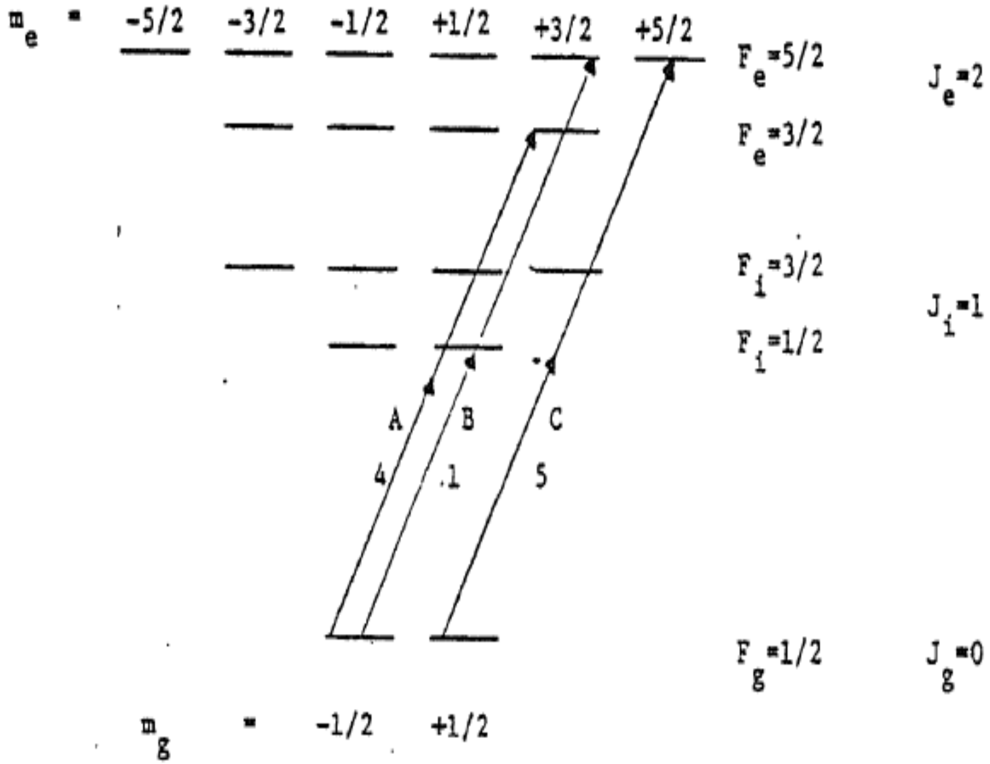
Single photon selection rules:
ΔF =0, +/-1
Δm_F= +1

Absorption length in air is ~4 mm, but 129.5 nm light is constantly generated by resonant and non resonant phase matched four wave mixing through the focal zone.

Polarized Xe 129 detection concepts

- Radar REMPI
  - Selectivity by spectral separation using 2+1 Radar REMPI
    - Requires suppression of background from molecular ionization (Chemring support)
    - 60 GHz linewidth and 7 GHz splitting limits the selectivity
  - Selectivity by microwave scattering polarization
  - Selectivity by 1+1 Radar REMPI from three photon polarization pumped upper state
- Laser Induced Fluorescence
  - Selectivity by polarization of 834.7 nm fluorescence (assuming no depolarization)
  - Possible backward amplification

Selection based on spectroscopy is a problem

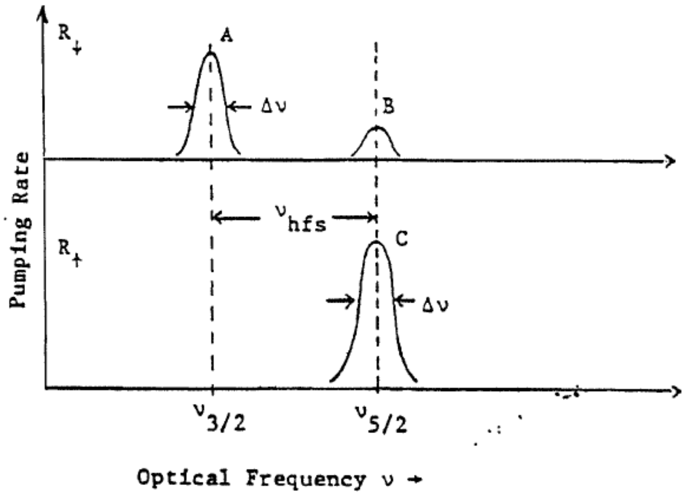


Influence of Pressure Broadening on the
Two-Photon Optical Pumping Efficiency of Xe^{129} in Air

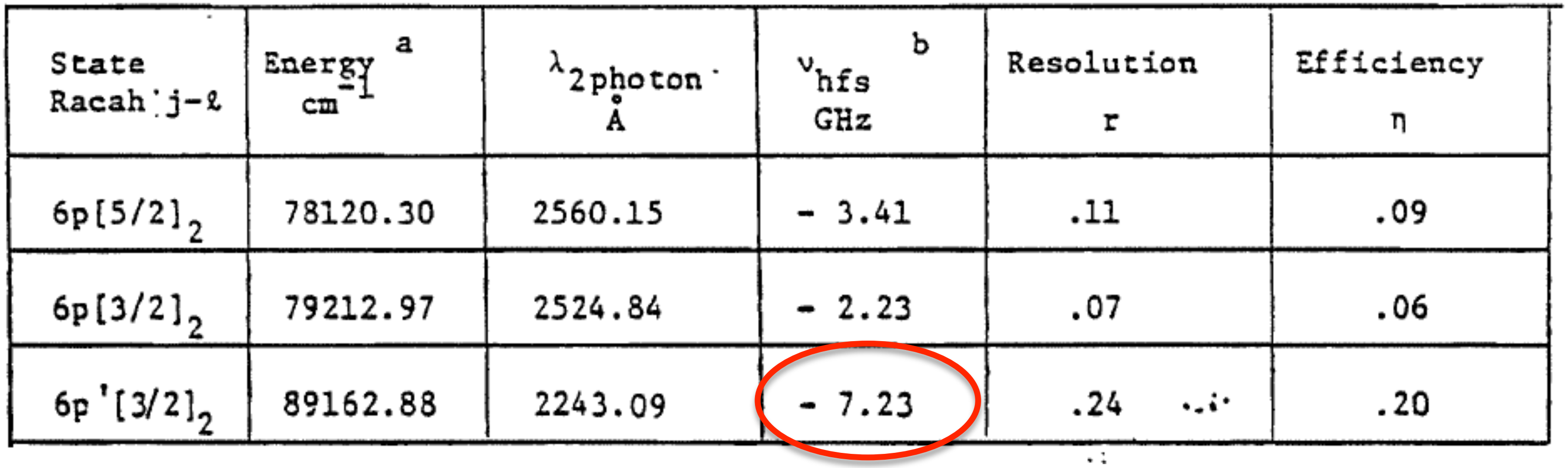
by W. Happer and Nam Tran

Pressure broadening does not allow effective spectral separation of F states

Separation of Hyperfine States

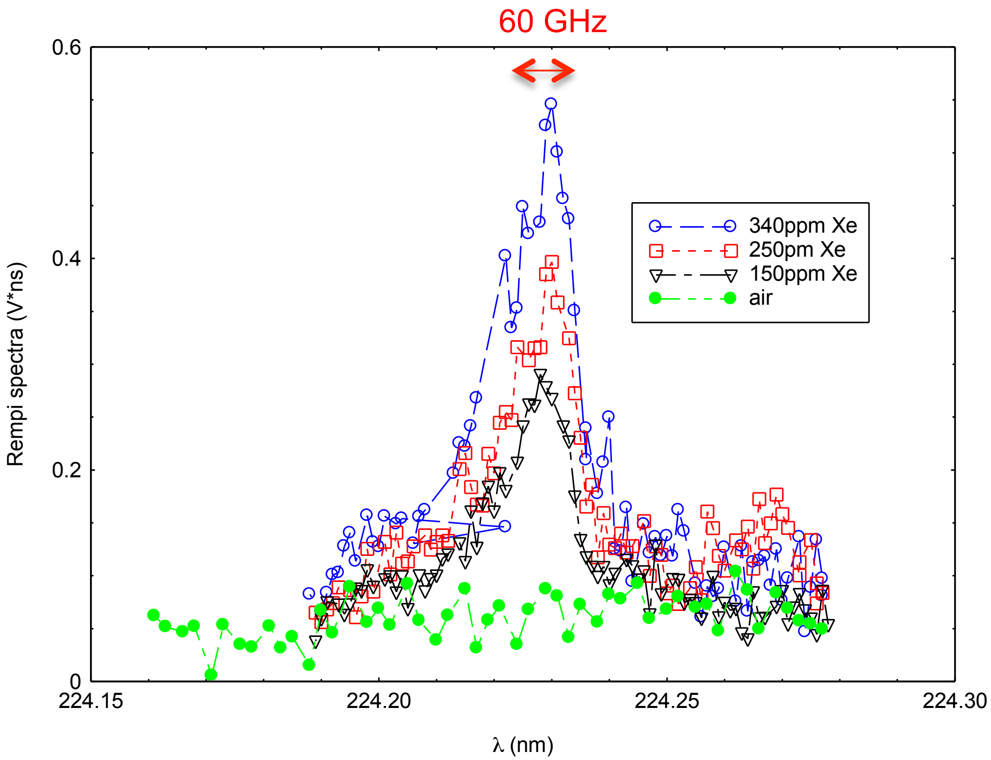


With full overlap, 3/2 and 1/2 states are not separable – the total line strength for each is the same



State Racah: j-ℓ	Energy^a cm^{-1}	$\lambda_{2photon}$ Å	ν_{hfs}^{b} GHz	Resolution r	Efficiency η
$6p[5/2]_2$	78120.30	2560.15	- 3.41	.11	.09
$6p[3/2]_2$	79212.97	2524.84	- 2.23	.07	.06
$6p'[3/2]_2$	89162.88	2243.09	- 7.23	.24	.20

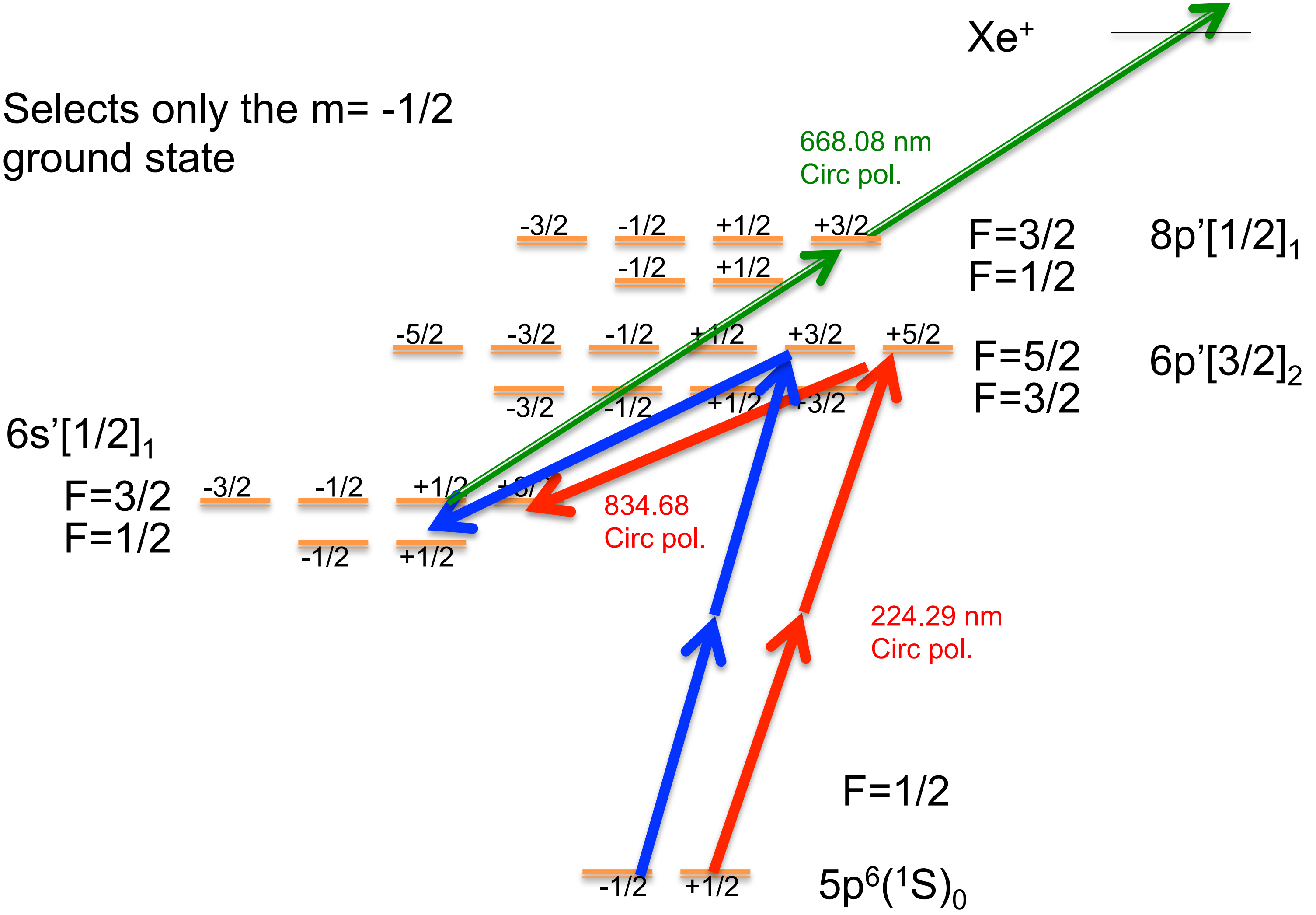
Radar REMPI Xe spectra in air



Spectra of the 6p’(3/2)$_2$ line for Xe in air.

Princeton University

Concept for Radar REMPI Interrogation of hyperpolarized xenon 129



Xe^+

Selects only the m= -1/2 ground state

668.08 nm
Circ pol.

-3/2 -1/2 +1/2 +3/2
-1/2 +1/2

F=3/2
F=1/2

$8p'[1/2]_1$

-5/2 -3/2 -1/2 +1/2 +3/2 +5/2
-3/2 -1/2 +1/2 +3/2

F=5/2
F=3/2

$6p'[3/2]_2$

$6s'[1/2]_1$

F=3/2
F=1/2

-3/2 -1/2 +1/2 +3/2
-1/2 +1/2

834.68
Circ pol.

224.29 nm
Circ pol.

F=1/2

-1/2 +1/2

$5p^6(^1S)_0$

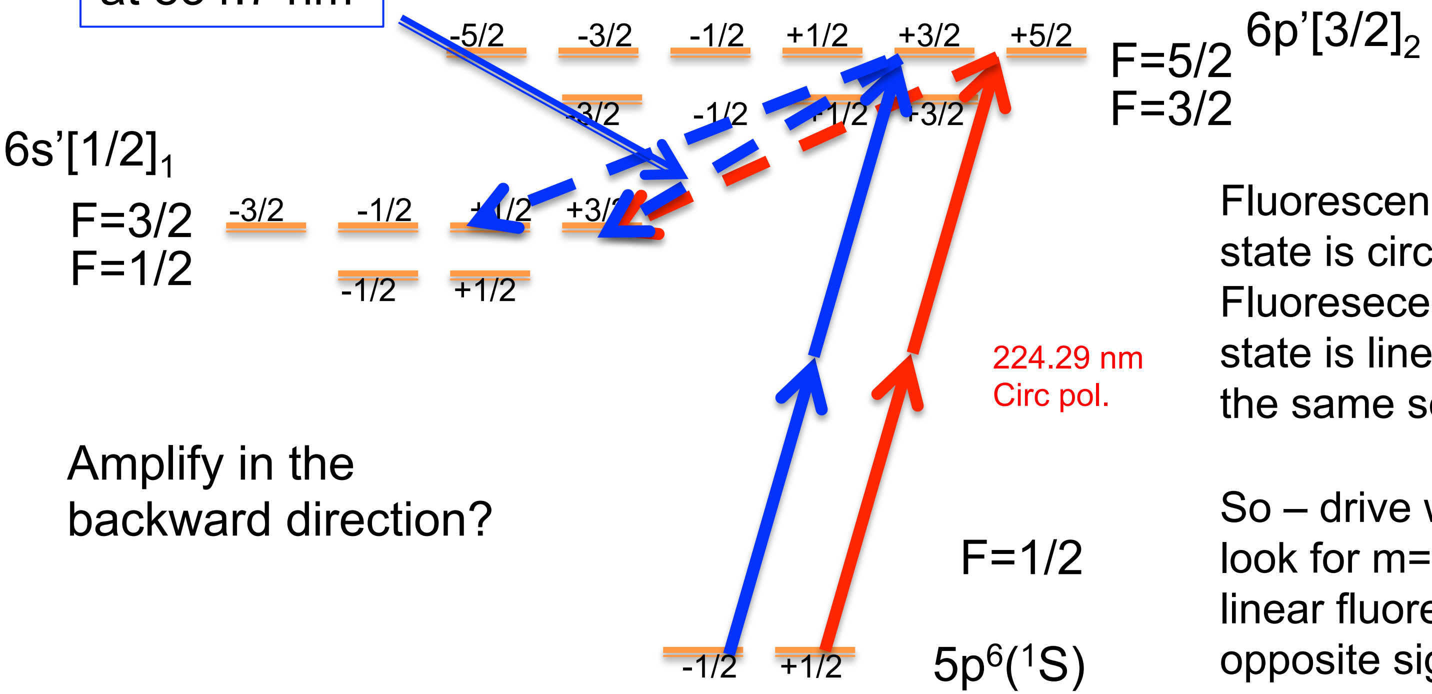
Princeton University

Features of 1+1 Radar REMPI of spin selected excited state

- High sensitivity due to 1+1 Radar REMPI
  - Nitric oxide is 1+1 Radar REMPI
- Negligible background ionization interference due to large separation from nitrogen and oxygen transitions
- Several wavelengths available depending on the intermediate state (eg. 826.65nm to 6p’$(1/2)_1$)
- Interference of parasitic ionization from spin selection step reduced by >10 nsec time delay of the 1+1 step
- No solar background

Fluorescence Interrogation of hyperpolarized xenon 129

Look for this at 834.7 nm



Amplify in the backward direction?

Fluorescence from m=+5/2 state is circular polarized Fluoresecence from m=+3/2 state is linear or circular with the same sense

So – drive with circular and look for m=+3/2 to m=+3/2 linear fluorescence (or opposite sign circularity) that selects only the m=-1/2 state

Summary Comments

- Radar REMPI has the sensitivity to detect parts per billion in the atmosphere
  - May be improved by higher power pulsed microwave, heterodyne detection and coherent detector array
  - May be improved by multiple laser ionization spots and coherent summation
  - May be improved for the detection of atomic species by fsec laser dissociation of nitrogen and oxygen, removing the background interference
- Xe ^{129} can be hyperpolarized by doubly resonant, circular polarized three photon pumping as well as by direct pumping by four wave mixing generated resonant circular polarized single photon absorption
- Spin polarization of Xe ^{129} can be detected by 1+1 circular polarized Radar REMPI from a spin selected state, populated by doubly resonant, circular polarized three photon pumping
- Location is determined by the laser focal volume
- Tracking by FLEET?

Tracking Air Motion by Femtosecond Laser Electronic Excitation Tagging (FLEET)

Applied Physics Group
Princeton University

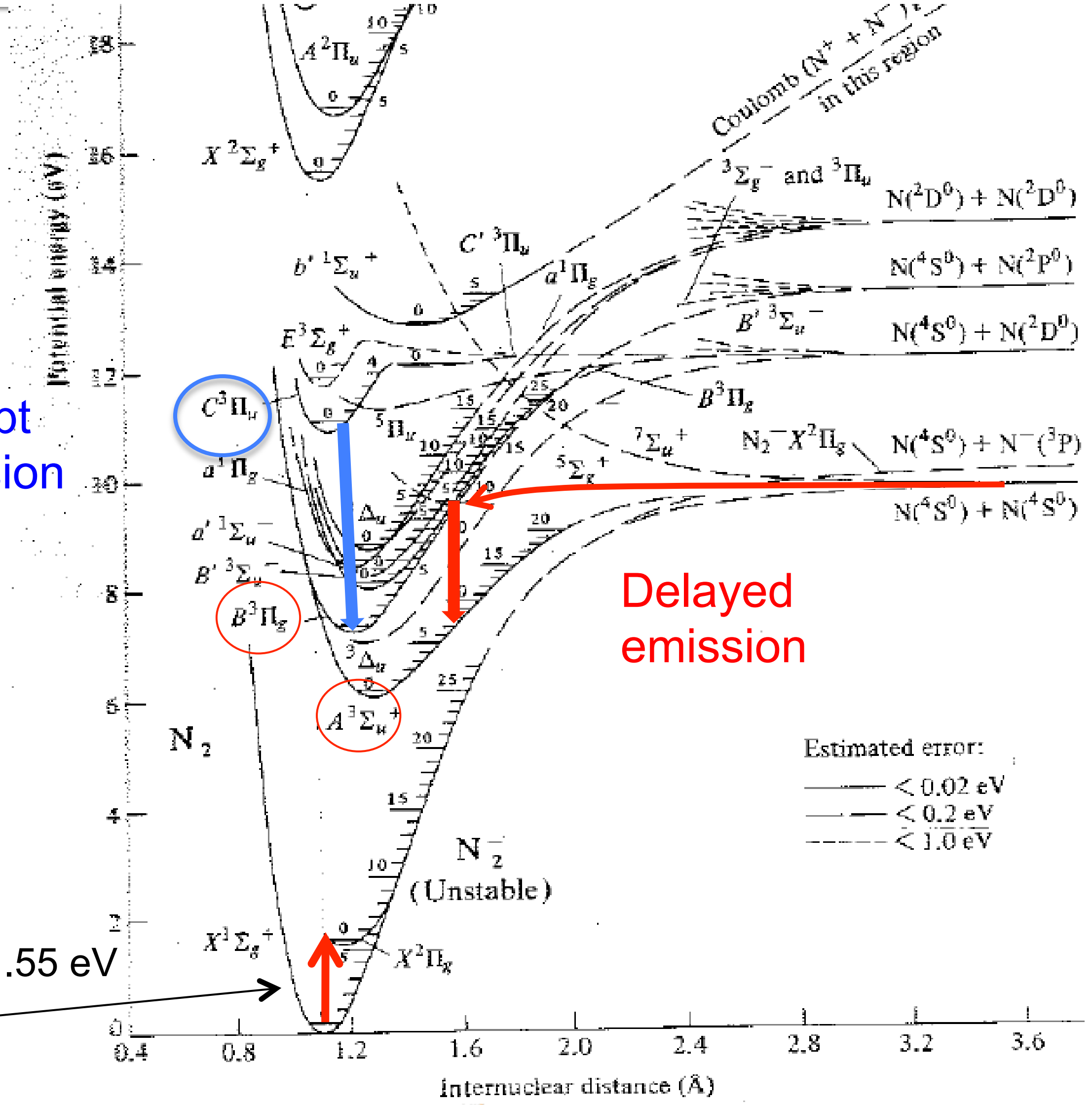
Molecular Tagging

- True measurement of flow (follows the molecules)
- Lines for velocity profiles
  - Instantaneous flow structure
  - Spatial correlations
  - Transverse structure functions
- Crosses for point vector velocity and vorticity
- Rectangles for shear stress and dilatation
- Two and three dimensional grids for full velocity field
- Rapid sequential imaging for flow evolution
- Placement and timing of the measurement is controlled by the writing laser
- Displacement can be viewed stereoscopically for three dimensional measurements
- Spatial resolution can be microns
- Non intrusive – no physical probe required
- No seeding if nitrogen is a component of the flow

FLEET Features

- One laser – no tuning required
- Time delayed camera
- Can follow the flow evolution with multiple images of the same tagged region
- Cross and grid patterns can be written easily
- Operational in humid air
- Works in combusting environments
- Strong signal even at low pressure
- Extensions
  - Spectrum can indicate the temperature and species present
  - Simultaneous Rayleigh scattering gives the density profile

Nitrogen Atom Recombination

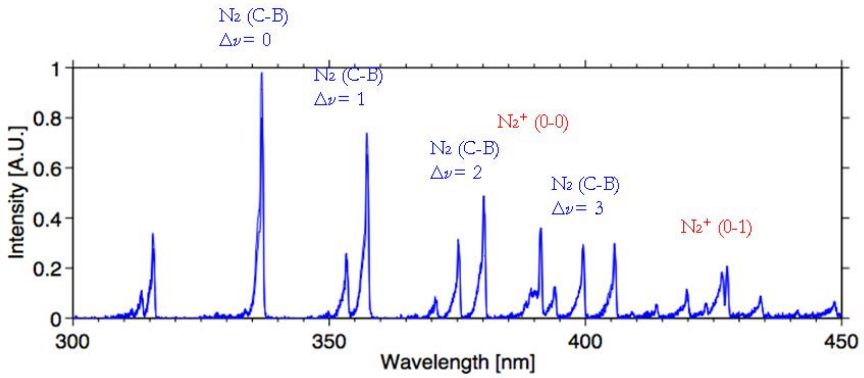


Prompt emission

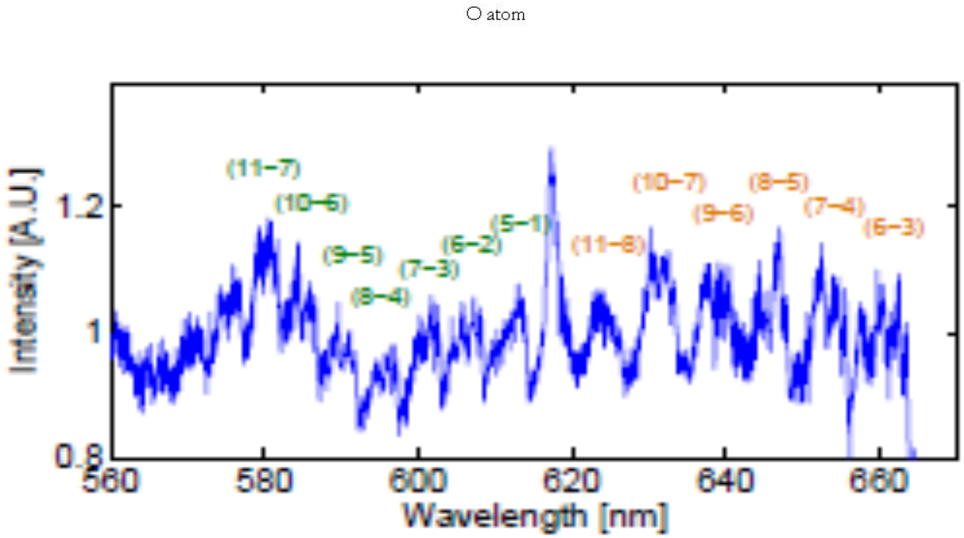
Delayed emission

800 nm = 1.55 eV

Spectra



Prompt –
Second positive band in air

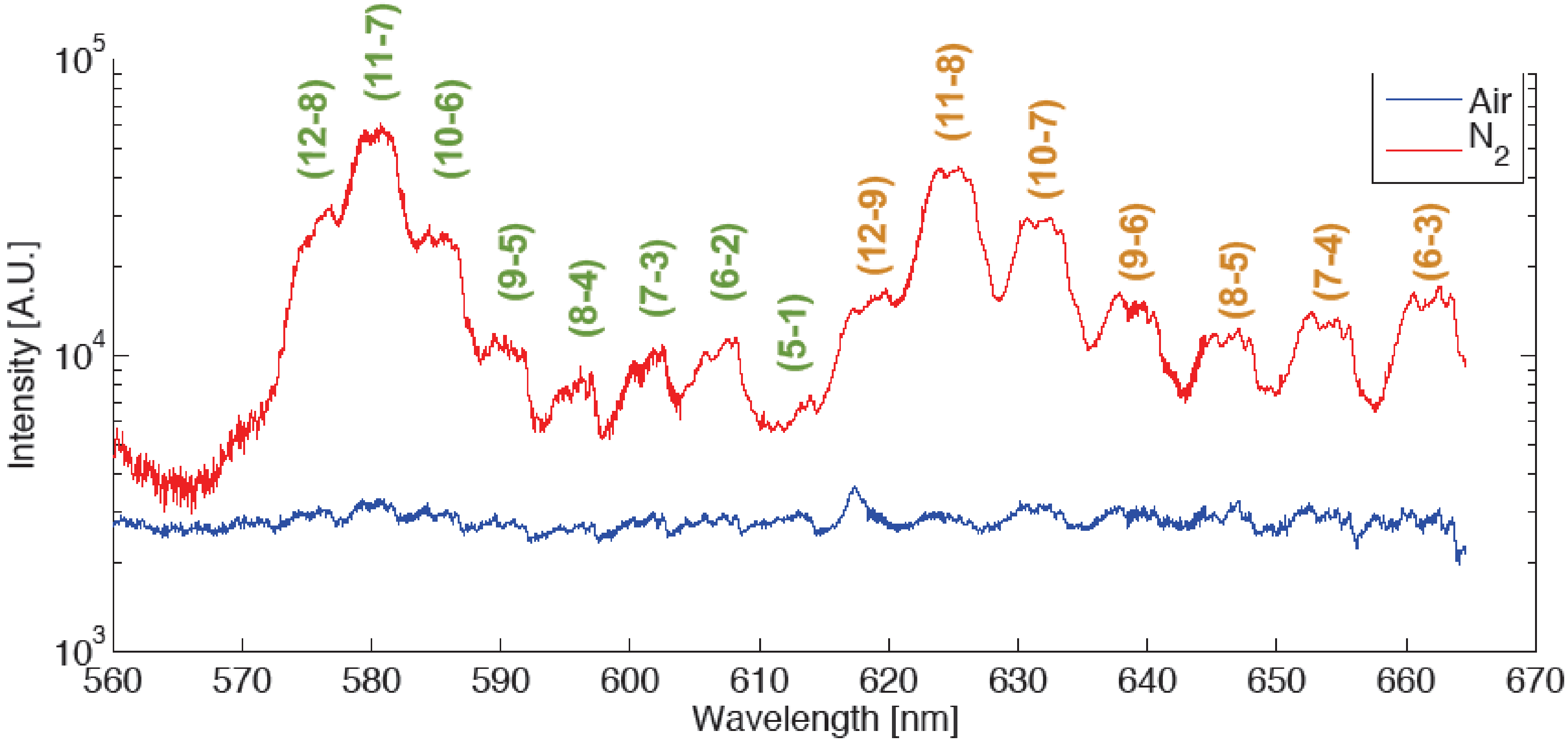


Delayed –
“Pink afterglow”
First positive band in air

Emission in Nitrogen and in Air

$$\mathrm{N}(^4\mathrm{S}) + \mathrm{N}(^4\mathrm{S}) + \mathrm{M} \longrightarrow \mathrm{N}_2(\mathrm{B}^3\Pi_g) + \mathrm{M}$$

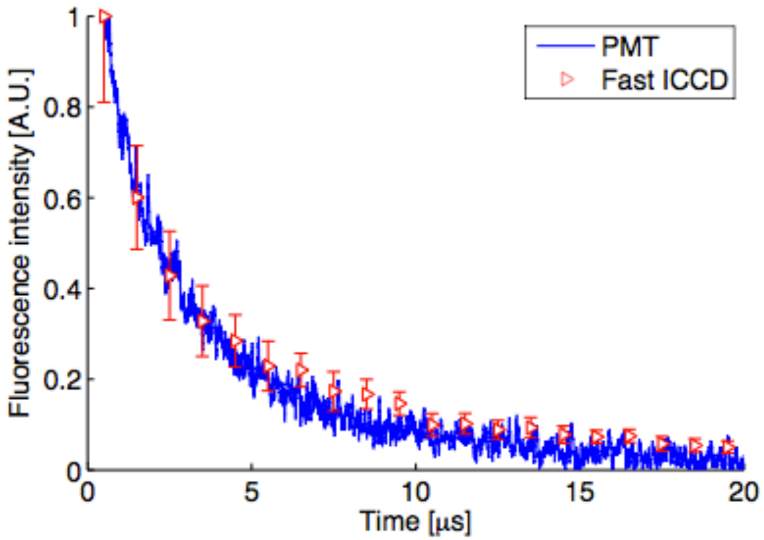
$$\mathrm{N}_2(\mathrm{B}^3\Pi_g, v') \longrightarrow \mathrm{N}_2(\mathrm{A}^3\Sigma_u^+, v'') + h\nu$$

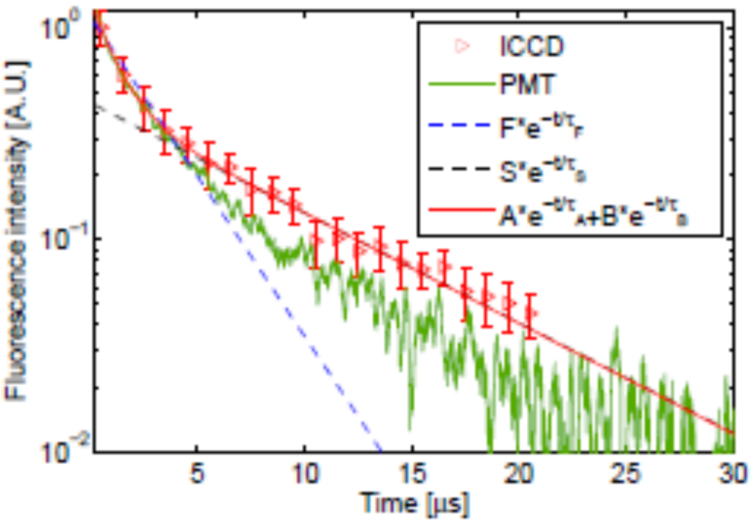


Princeton University

ONR
Revolutionary Research . . . Relevant Results

Fluorescence Lifetime

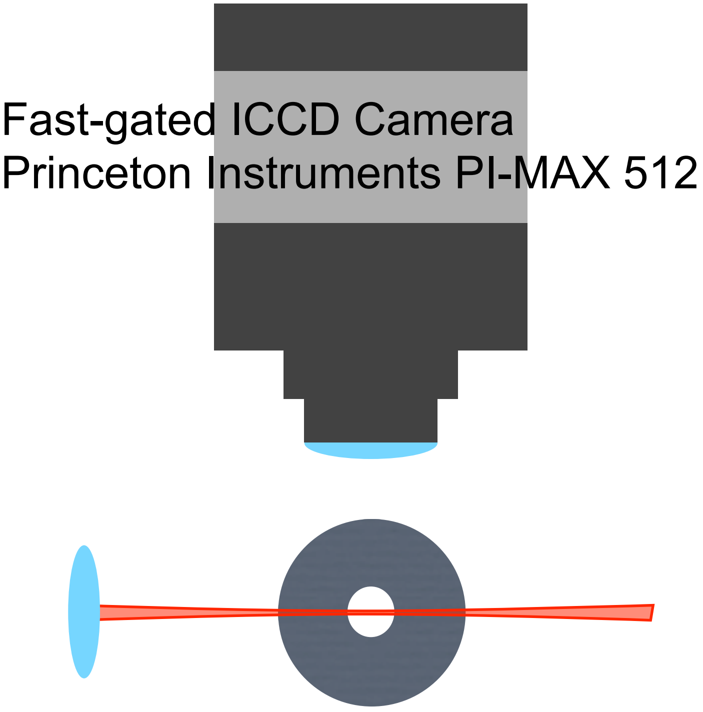




Double exponential
1.1 μsec fast decay
8.3 μsec slow decay

FLEET Experimental setup

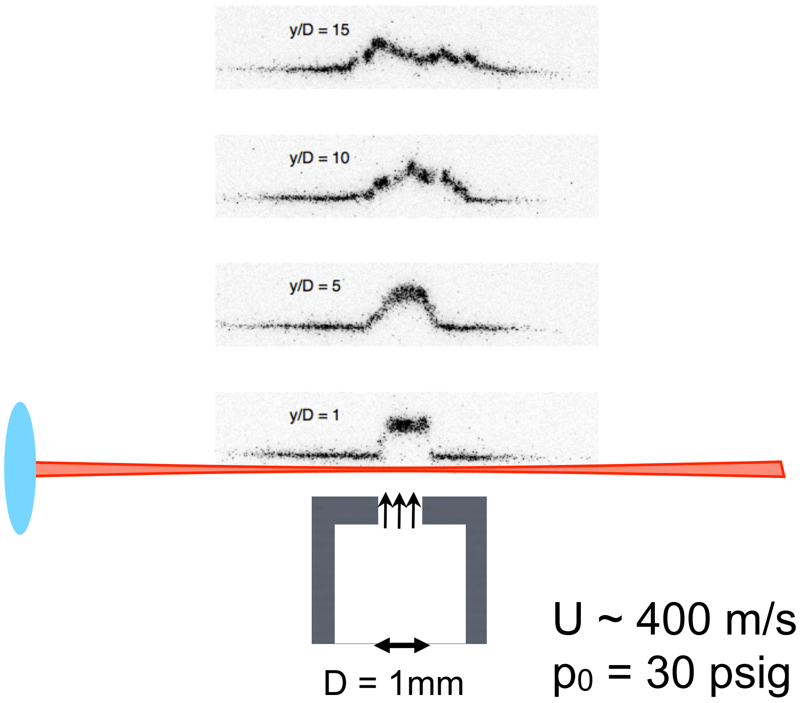
Top View



Fast-gated ICCD Camera
Princeton Instruments PI-MAX 512

Laser: ~150 fs, 800 nm, 1.2 mJ

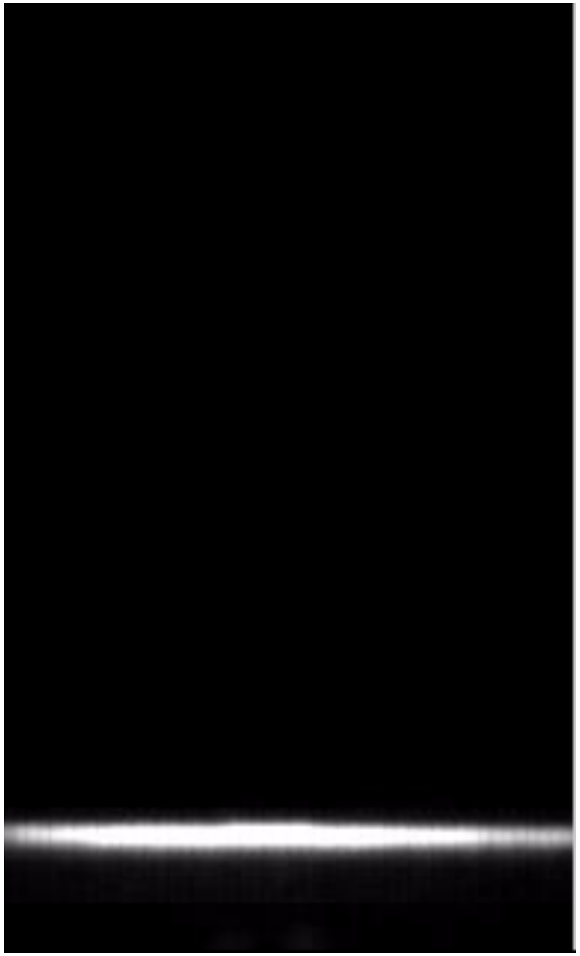
Side View



D = 1mm

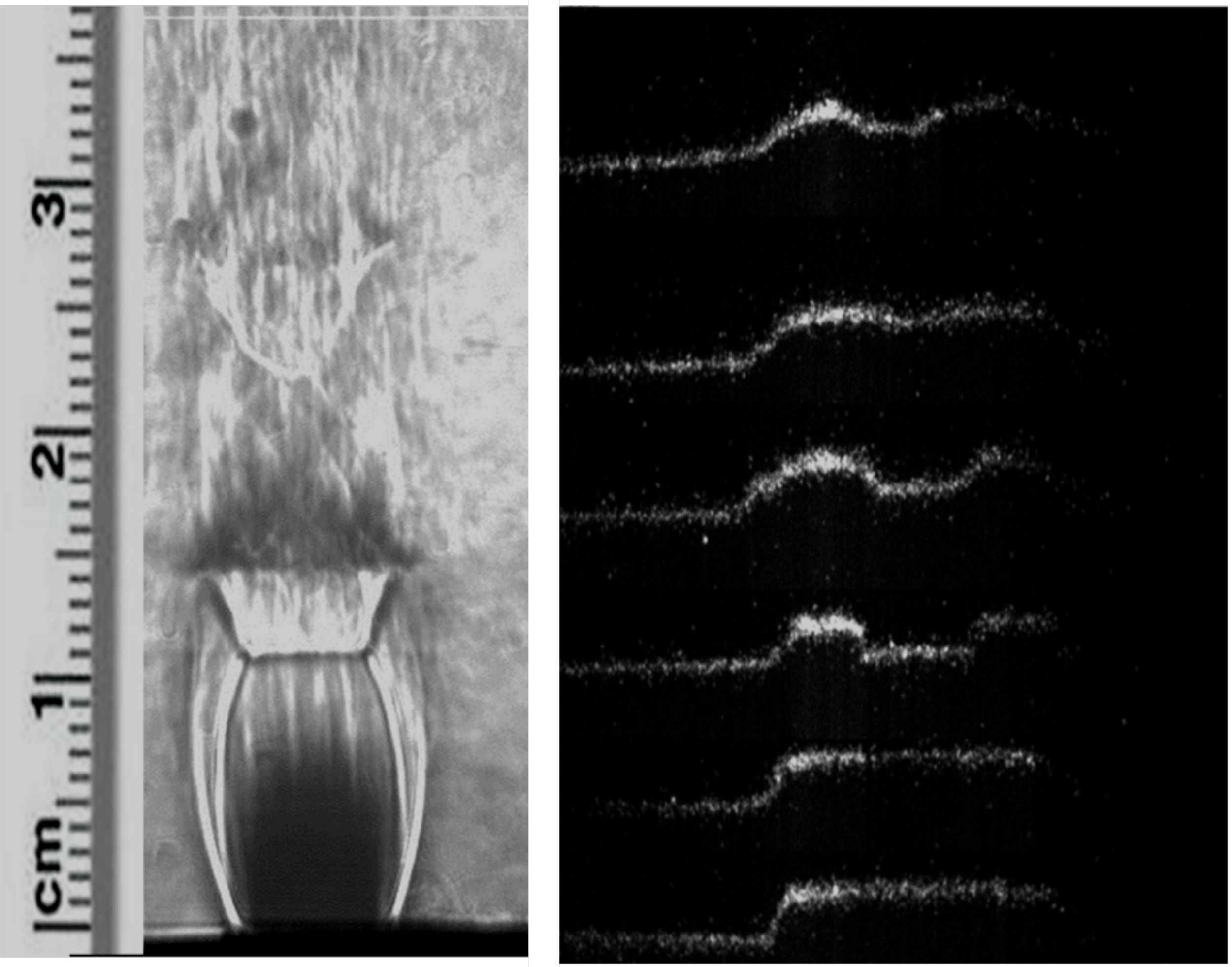
U ~ 400 m/s
p_0 = 30 psig

Subsonic Demonstration Video



- "Dead space" between laser pulses is removed for presentation
- Each progression includes about 10 line displacement shots due to the long lifetime in pure N2
- Measured centerline velocity ~150m/s

FLEET in Supersonic flow



FLEET Characteristics

- No seeding required
- Operates in air and nitrogen and other gas mixtures containing nitrogen
- Instantaneous profiles
- No intrusive probe required
- High resolution (better than 40 microns)
- Simplicity (one laser and one camera)
- Grids and crosses give vorticity and shear stresses
- Operation at pressures as low as 1 Torr to > 1 atm
- Operation at temperatures from condensation to combustion (<100K to > 2000K)
- Operation with combustion products (water vapor, etc)
- May provide temperature profiles
- May provide species profiles
- May provide density profiles