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14. ABSTRACT

Iodine (I_2) has been discussed seriously as a propellant for Hall effect and other electrostatic thrusters as early as 2000. Atomic iodine has a mass of 126.9 amu, but as a halogen the natural state is diatomic (I_2) with a molecular mass of 253.8 amu. Atomic iodine (I) only has an ionization energy of 10.45 eV. The density of iodine (solid at room temperature) is 4.933 g/cc. Iodine also has a relatively high vapor pressure at low temperatures. Vapor pressures of 100 Pa are achieved at only 39°C. It appears obvious that the spacecraft community could greatly benefit from a propellant with nearly the atomic characteristics as xenon, but with a lower ionization potential. In addition, iodine is approximately 100× less expensive and more abundant than xenon while exhibiting better gasification characteristics than other condensable propellants such as bismuth. Iodine appears to offer the benefits of cryogenic propellant storage without the need for active cooling or insulation, and only a moderate heating requirement for gasification (183 °C yields 1 atm). A propellant storage system for iodine this therefore believed to have mass fractions of less than 1%. While laboratory evaluations of iodine in an operational electrostatic plasma thruster are limited, the results are very promising. Performance appears to be on par with xenon without significant modification of the thruster. Intriguingly, performance appears to rise and exceed xenon at higher discharge potentials. The extent to which these behaviors continue above the limits of the initial studies is unknown, but is under active investigation and one active effort is focused on construction of a full system to demonstrate an iodine Hall effect thruster system. All of these issues must be addressed to determine potential performance gains over state of the art xenon thrusters and potential spacecraft interactions. While many of the probe based diagnostics customarily used to diagnose the plumes of plasma thrusters can and have provided valuable insights into iodine thruster plasma acceleration; optical diagnostics can provide unparalleled nonintrusive resolution of the plasma acceleration with sub-mm resolution. This effort presents the demonstration of iodine ion laser-induced fluorescence (LIF) for detailed measurements of the plasma acceleration process.

15. SUBJECT TERMS

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Laser-Induced Fluorescence of the Iodine Ion

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Outline

- Iodine as a Hall effect thruster propellant
- Singly ionized atomic iodine (2^{nd} spectrum)
- Selection/Analysis of a suitable transition
- Table top experimental efforts
- Conclusions
- Future work

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Alternative HET Propellants: Iodine as a Propellant?

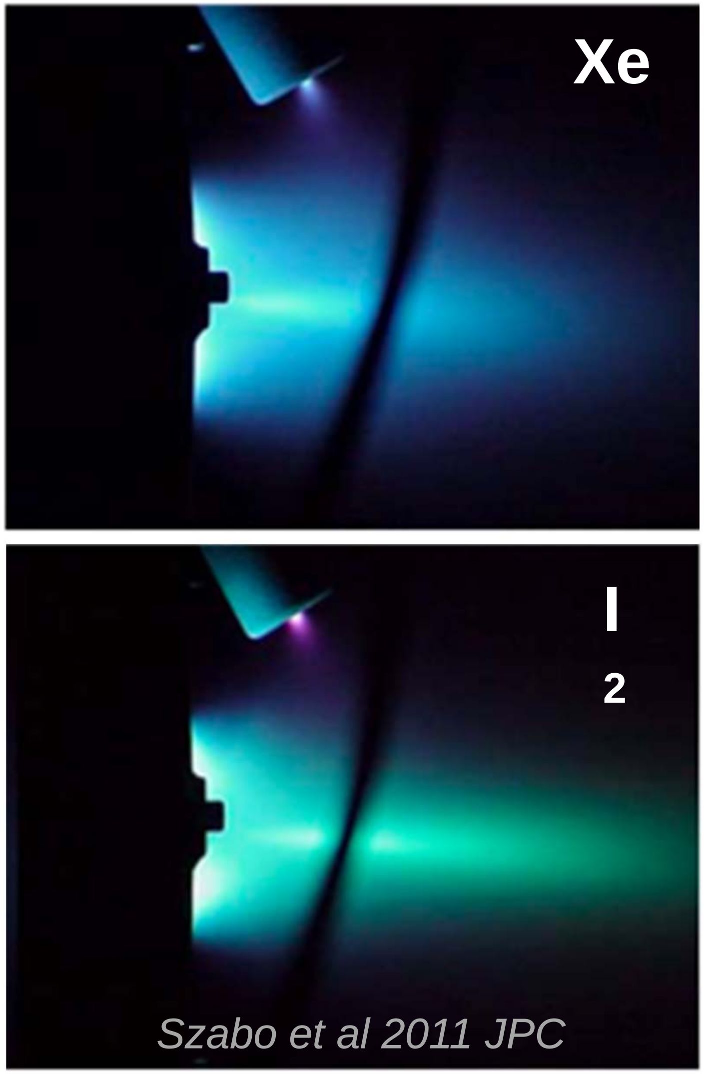
- **Iodine is a demonstrated HET propellant**
  - **Cheaper than xenon, similar critical properties**
  - **3x higher storage density**
  - **Low pressure storage**
- **Issues / unknowns with iodine**
  - **Vapor pressure requires temperature control**
  - **New flow control system design/complexity**
  - **Performance and lifetime?**
  - **Safety?**

Xe

Noble Gas
131.3 amu
Ionization energies:
12 eV, 21 eV, 32 eV
1.4 g/cc at 3 kpsi

I_2

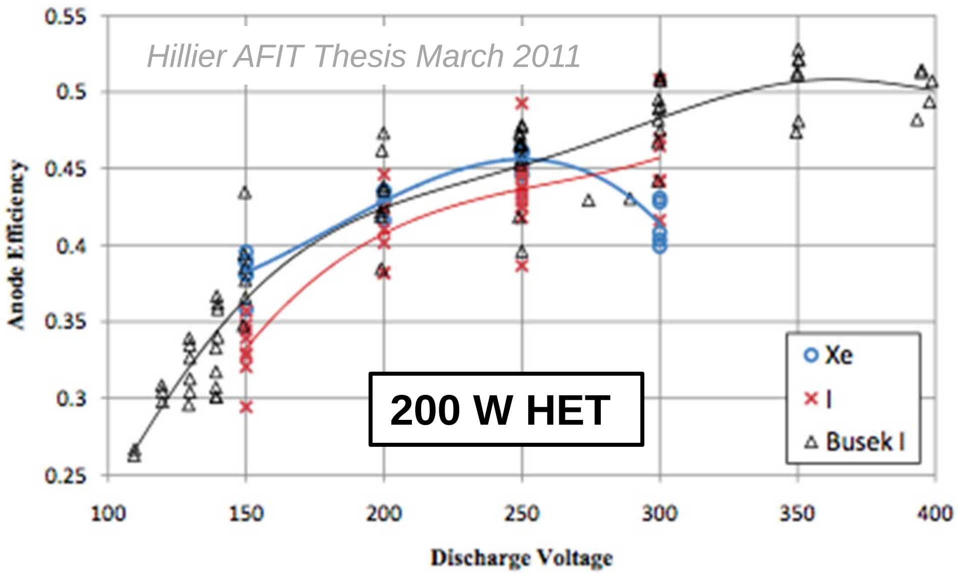
Solid Halogen
126.9 amu
Atomic Ionization:
10 eV, 19 eV, ?? eV
4.9 g/cc solid



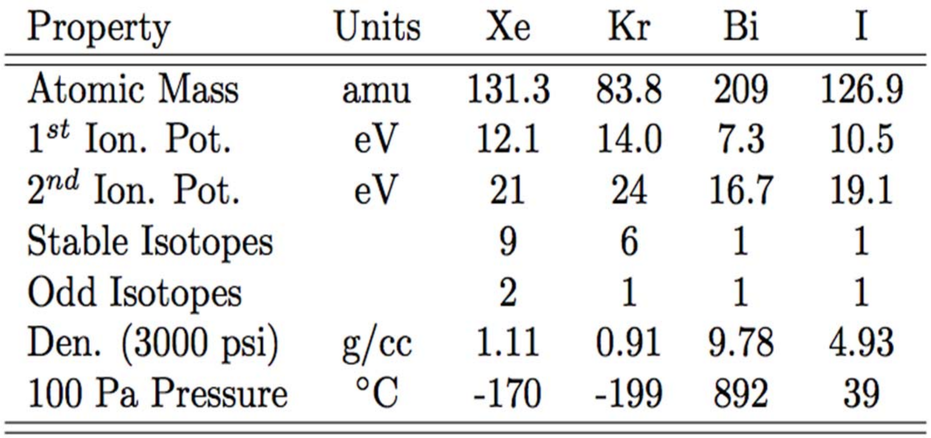
Szabo et al 2011 JPC

Comparison of Alternative Propellants

- **Iodine compared to other propellants**
  - **Atomic mass (127 amu)**
  - **Molecular mass (254 amu)**
  - **Relatively high pressure (for solid)**
- **Needs for iodine flow system**
  - **heating**
  - **Flow metering**
  - **Flow control**


Hillier AFIT Thesis March 2011

200 W HET



Property	Units	Xe	Kr	Bi	I
Atomic Mass	amu	131.3	83.8	209	126.9
1^{st} Ion. Pot.	eV	12.1	14.0	7.3	10.5
2^{nd} Ion. Pot.	eV	21	24	16.7	19.1
Stable Isotopes		9	6	1	1
Odd Isotopes		2	1	1	1
Den. (3000 psi)	g/cc	1.11	0.91	9.78	4.93
100 Pa Pressure	°C	-170	-199	892	39

- **Iodine HET studies at Busek**
  - **Joint effort AFRL/RV/RZ & AFIT**
    - **Hillier AFIT thesis**
    - **Szabo, et al (JPC 2011, JPP 2012)**
  - **Successful operation on 200 W HET**
- **Iodine HET performance**
  - **Meets or exceeds Xe performance**
  - **High eff. at high accel. Potentials**

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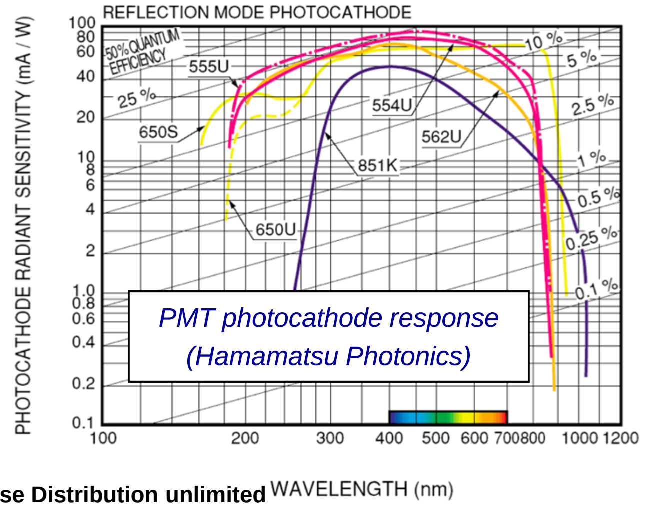
Considerations for Identification of Suitable Transitions

- **Transition wavelength laser accessibility**
  - Laser types
    - Dye – laboratory work horses
    - Solid state – less messy, more limited
    - Diode – easier to work with, wavelength limited
  - Tunable diode lasers
    - Broad tuning capabilities
    - Low maintenance requirements
    - Limited to available band gaps
    - Typically ~400 nm & 650-1500 nm
  - Limits interrogation to excited states
- **Sufficiently populated lower state**
  - Non-equilibrium plasma
  - Neutral / ion temperatures not clearly defined
  - Meta-stable states!
    - Optical relaxation QM not allowed
    - Collisional de-excitation is allowed
    - Long radiative lifetimes (seconds)
    - Collisional de-excitation is allowed
- **Fluorescence transition selection**
  - Resonant
    - Detection at same wavelength as excitation
  - Non-resonant
    - Detection of alternative transitions from excited state
    - Less prone to interference due to reflection
  - Considerations
    - Branching ratios of excited state fluorescence
    - Detector QE (blue-visible preferred)
    - Interference from near by transitions
    - Typically ~400 nm & 650-1500 nm



PMT photocathode response (Hamamatsu Photonics)

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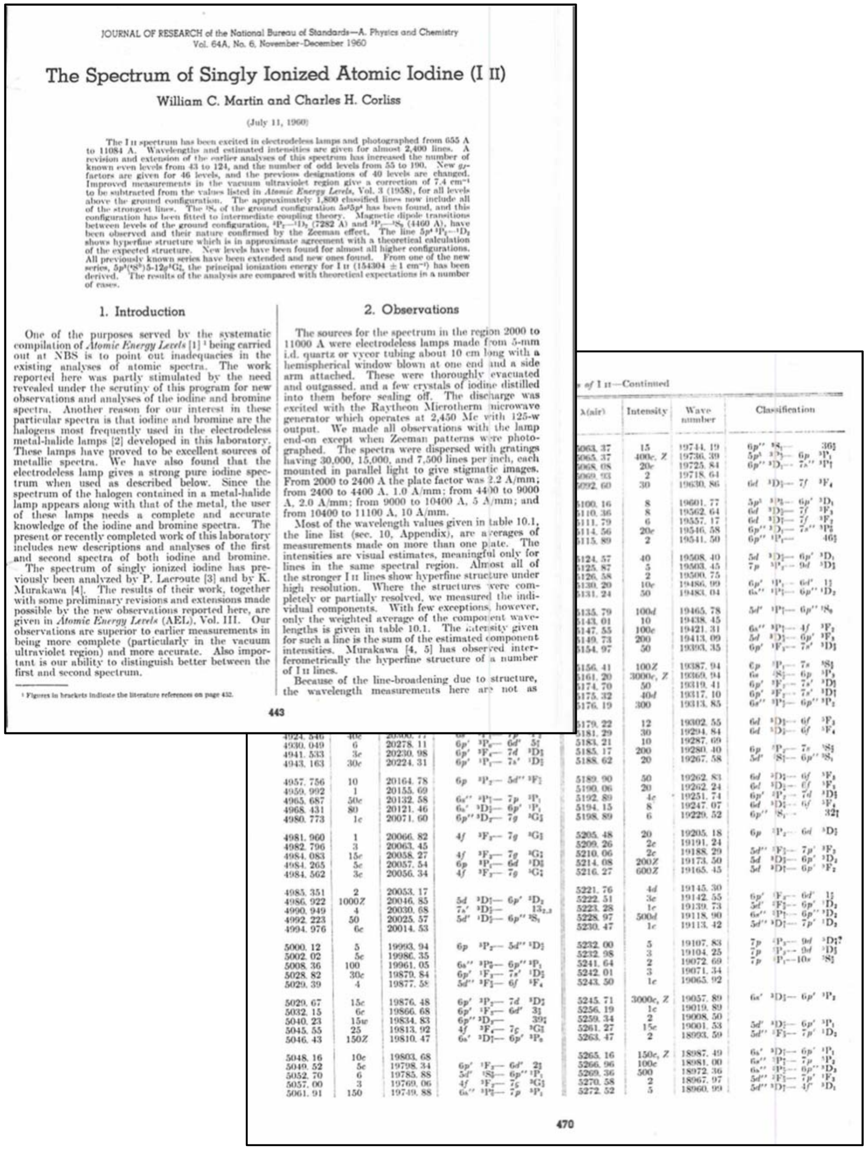
Alternative HET Propellants:
I II Transition Identification



JOURNAL OF RESEARCH of the National Bureau of Standards—A. Physics and Chemistry
Vol. 64A, No. 6, November-December 1960

The Spectrum of Singly Ionized Atomic Iodine (I II)

William C. Martin and Charles H. Corliss

(July 11, 1960)

The I II spectrum has been excited in electrodeless lamps and photographed from 655 A to 11084 A. Wavelengths and estimated intensities are given for almost 2,400 lines. A revision and extension of the earlier analyses of this spectrum has increased the number of known even levels from 43 to 124, and the number of odd levels from 55 to 190. New g_J-factors are given for 46 levels, and the previous designations of 40 levels are changed. Improved measurements in the vacuum ultraviolet region give a correction of 7.4 cm^{-1} to be subtracted from the values listed in *Atomic Energy Levels*, Vol. 3 (1958), for all levels above the ground configuration. The approximately 1,800 classified lines now include all of the strongest lines. The $^1S_0$ of the ground configuration $5s^25p^4$ has been found, and this configuration has been fitted to intermediate coupling theory. Magnetic dipole transitions between levels of the ground configuration, $^3P_2$—$^1D_2$ (7282 A) and $^3P_1$—$^1S_0$ (4460 A), have been observed and their nature confirmed by the Zeeman effect. The line $5p^4\,^3P_2$—$^1D_2$ shows hyperfine structure which is in approximate agreement with a theoretical calculation of the expected structure. New levels have been found for almost all higher configurations. All previously known series have been extended and new ones found. From one of the new series, $5p^3(^4S^\circ)5\text{-}12g\,^5G^\circ_{\frac{?}{2}}$, the principal ionization energy for I II (154304 ± 1 cm^{-1}) has been derived. The results of the analysis are compared with theoretical expectations in a number of cases.

1. Introduction

One of the purposes served by the systematic compilation of *Atomic Energy Levels* [1] [1] being carried out at NBS is to point out inadequacies in the existing analyses of atomic spectra. The work reported here was partly stimulated by the need revealed under the scrutiny of this program for new observations and analyses of the iodine and bromine spectra. Another reason for our interest in these particular spectra is that iodine and bromine are the halogens most frequently used in the electrodeless metal-halide lamps [2] developed in this laboratory. These lamps have proved to be excellent sources of metallic spectra. We have also found that the electrodeless lamp gives a strong pure iodine spectrum when used as described below. Since the spectrum of the halogen contained in a metal-halide lamp appears along with that of the metal, the user of these lamps needs a complete and accurate knowledge of the iodine and bromine spectra. The present or recently completed work of this laboratory includes new descriptions and analyses of the first and second spectra of both iodine and bromine.

The spectrum of singly ionized iodine has previously been analyzed by P. Lacroute [3] and by K. Murakawa [4]. The results of their work, together with some preliminary revisions and extensions made possible by the new observations reported here, are given in *Atomic Energy Levels* (AEL), Vol. III. Our observations are superior to earlier measurements in being more complete (particularly in the vacuum ultraviolet region) and more accurate. Also important is our ability to distinguish better between the first and second spectrum.

2. Observations

The sources for the spectrum in the region 2000 to 11000 A were electrodeless lamps made from 5-mm i.d. quartz or vycor tubing about 10 cm long with a hemispherical window blown at one end and a side arm attached. These were thoroughly evacuated and outgassed. and a few crystals of iodine distilled into them before sealing off. The discharge was excited with the Raytheon Microtherm microwave generator which operates at 2,450 Mc with 125-w output. We made all observations with the lamp end-on except when Zeeman patterns were photographed. The spectra were dispersed with gratings having 30,000, 15,000, and 7,500 lines per inch, each mounted in parallel light to give stigmatic images. From 2000 to 2400 A the plate factor was 2.2 A/mm; from 2400 to 4400 A, 1.0 A/mm; from 4400 to 9000 A, 2.0 A/mm; from 9000 to 10400 A, 5 A/mm; and from 10400 to 11100 A, 10 A/mm.

Most of the wavelength values given in table 10.1, the line list (sec. 10, Appendix), are averages of measurements made on more than one plate. The intensities are visual estimates, meaningful only for lines in the same spectral region. Almost all of the stronger I II lines show hyperfine structure under high resolution. Where the structures were completely or partially resolved, we measured the individual components. With few exceptions, however, only the weighted average of the component wavelengths is given in table 10.1. The intensity given for such a line is the sum of the estimated component intensities. Murakawa [4, 5] has observed interferometrically the hyperfine structure of a number of I II lines.

Because of the line-broadening due to structure, the wavelength measurements here are not as

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[1] Figures in brackets indicate the literature references on page 432.

443

- **Second spectrum of iodine**
  - I^+
  - I II
  - Not I_2, I_2^+…
- **Only 1 study of the second spectrum**
  - Martin and Corliss, NBS J. 1960.
  - Only partially analyzed by NIST
- **Quantities required for a "good" transition (ideally)**
  - Ground state not accessible
  - Need to find a metastable state
  - Need to find all related transitions
  - Need to verify that these transitions actually exist (no guaranties)

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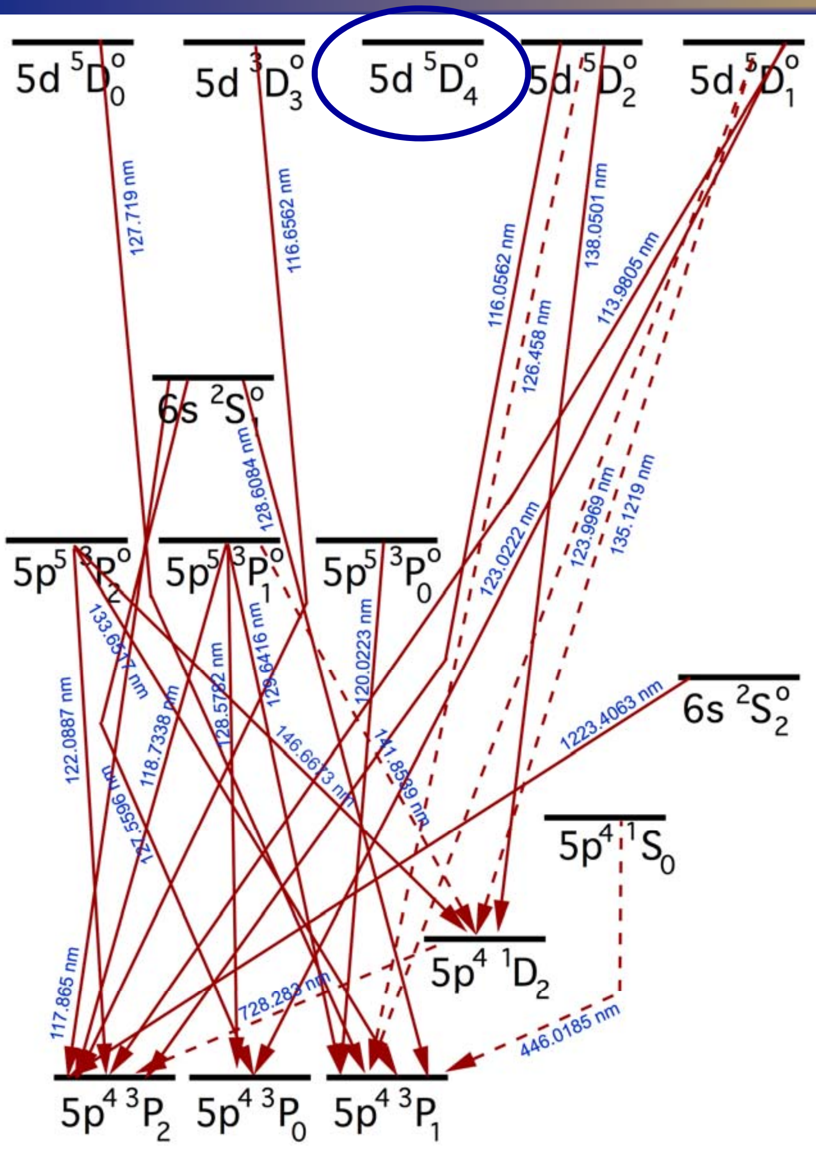
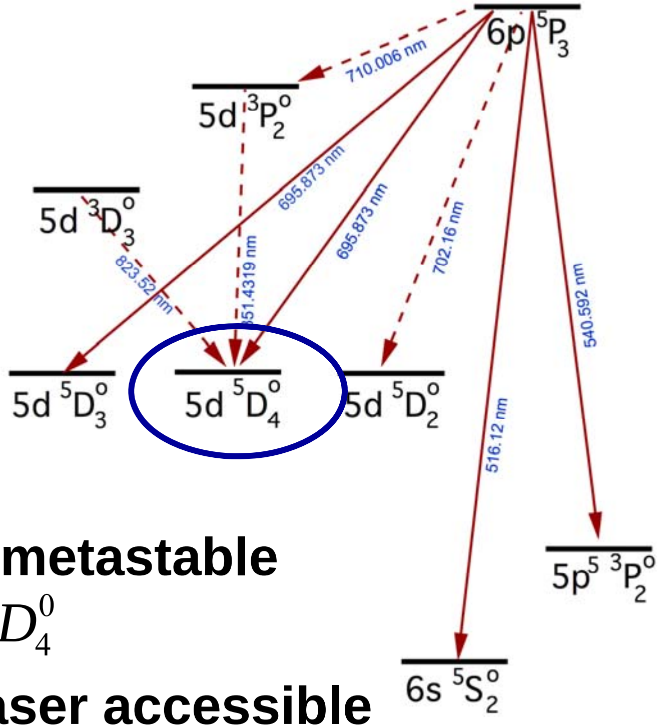
Alternative HET Propellants: I II Transition Identification





Identified metastable state! $5d^5D_4^0$

…with a laser accessible transition at 695.9 nm

$$5d^5D_4^0 \rightarrow 6p^5P_3$$

…and non-resonant fluorescence at 516.2 nm

$$6s^5S_2^0 \rightarrow 6p^5P_3$$

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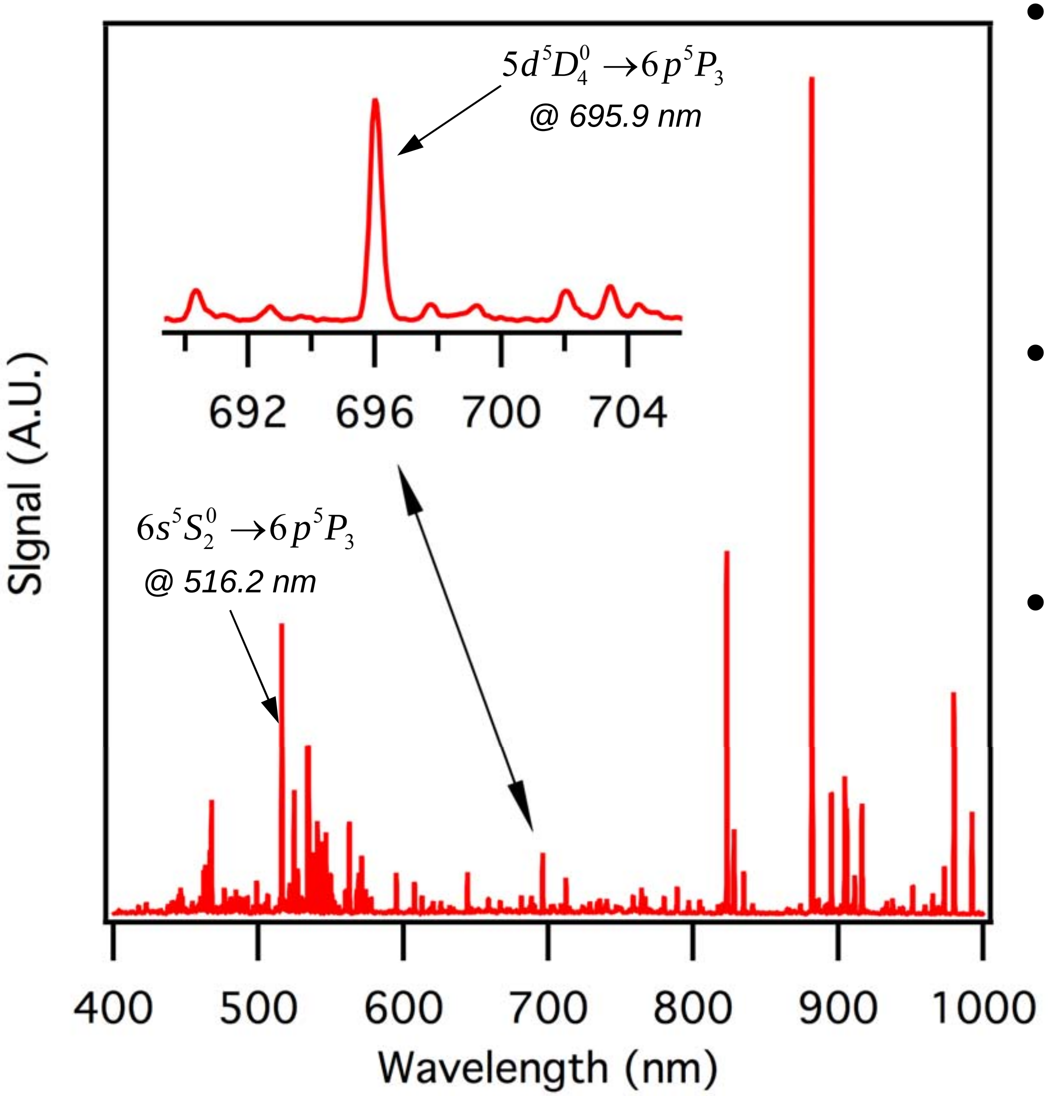
Iodine HET Emission Spectrum:

Courtesy of Prince and Chiu (AIAA-2012-3872)



$5d^5D_4^0 \rightarrow 6p^5P_3$

@ 695.9 nm

$6s^5S_2^0 \rightarrow 6p^5P_3$

@ 516.2 nm

- **Emission spectrum available**
  - **Courtesy of Prince & Chiu**
  - **AIAA-2012-3872**
  - **Near plume**
  - **Note xenon in plume (NIR)**
- **Only 1 study of the second spectrum**
  - **Martin and Corliss (1956)**
  - **Only partially analyzed by NIST**
- **Quantities required for a "good" transition (ideally)**
  - **Ground state not accessible**
  - **Need to find a metastable state**
  - **Need to find all related transitions**
  - **Need to verify that these transitions actually exist (no guaranties)**

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Hyperfine Spin Splitting:
Nuclear Spin Complicates the Line Shape

- **Hyperfine spin-splitting**
  - **Causes (Iodine has 53 protons, 74 neutrons)**
    - **Single stable isotope with odd number of neutrons and protons I^{127}**
    - **Non-zero nuclear spin couples to angular momentum of atom/ion producing additional energy states**
  - **Require empirical data to model the transition line shape**
    - **Empirical data required**
    - **No known hyperfine data**
    - **Typically derived from nuclei structure studies**
  - **Issues**
    - **No known hyperfine data for 695.9 nm transition**
    - **Width of line shape could preclude useful measurements (s transitions are problematic…)**

If odd number of protons or neutrons, then nuclear spin couples is angular momentum J to produce additional non-degenerate energy states

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Hyperfine Spin Splitting

- **Total angular momentum: $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$**
  - Angular momentum $\boldsymbol{J}$ of atom is no longer sufficient
  - Nuclear spin $\boldsymbol{I}$ is coupled to $\boldsymbol{J}$
  - Total angular momentum is now $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$
  - Individual values of F are given by

$$\boxed{F = J + I, J + I - 1, \ldots, |J - I|}$$

- **Selection Rules**
  - Transitions between F values of upper/lower states

$$\Delta F = 0, \pm 1 \qquad \Delta F \neq 0\,,\ \text{if } F = 0$$

- **Energy separation of spin split states**
  - Constant A is a function of magnetic dipole moment

$$\Delta E_M(F) = \frac{1}{2}A[F(F+1) - J(J+1) - I(I+1)] = \frac{A}{2}C$$

  - For $I \geq 1$ electric quadrapole moments also present

$$\boxed{\Delta E_F = \Delta E_M + \Delta E_Q = \frac{AC}{2} + B\left[C(C+1) - \frac{4}{3}J(J+1)I(I+1)\right]}$$

  - Constants A and B derived from experimental data…

- **Component intensities**
  - Very close energy spacing
  - Russell-Saunders (LS) coupling holds
  - Example for $J = J'$

$$F - 1 \rightarrow F : S = -\kappa\frac{(J+F+I+1)(J+F-I)(J-F+I+1)(J-F-I)}{F}$$

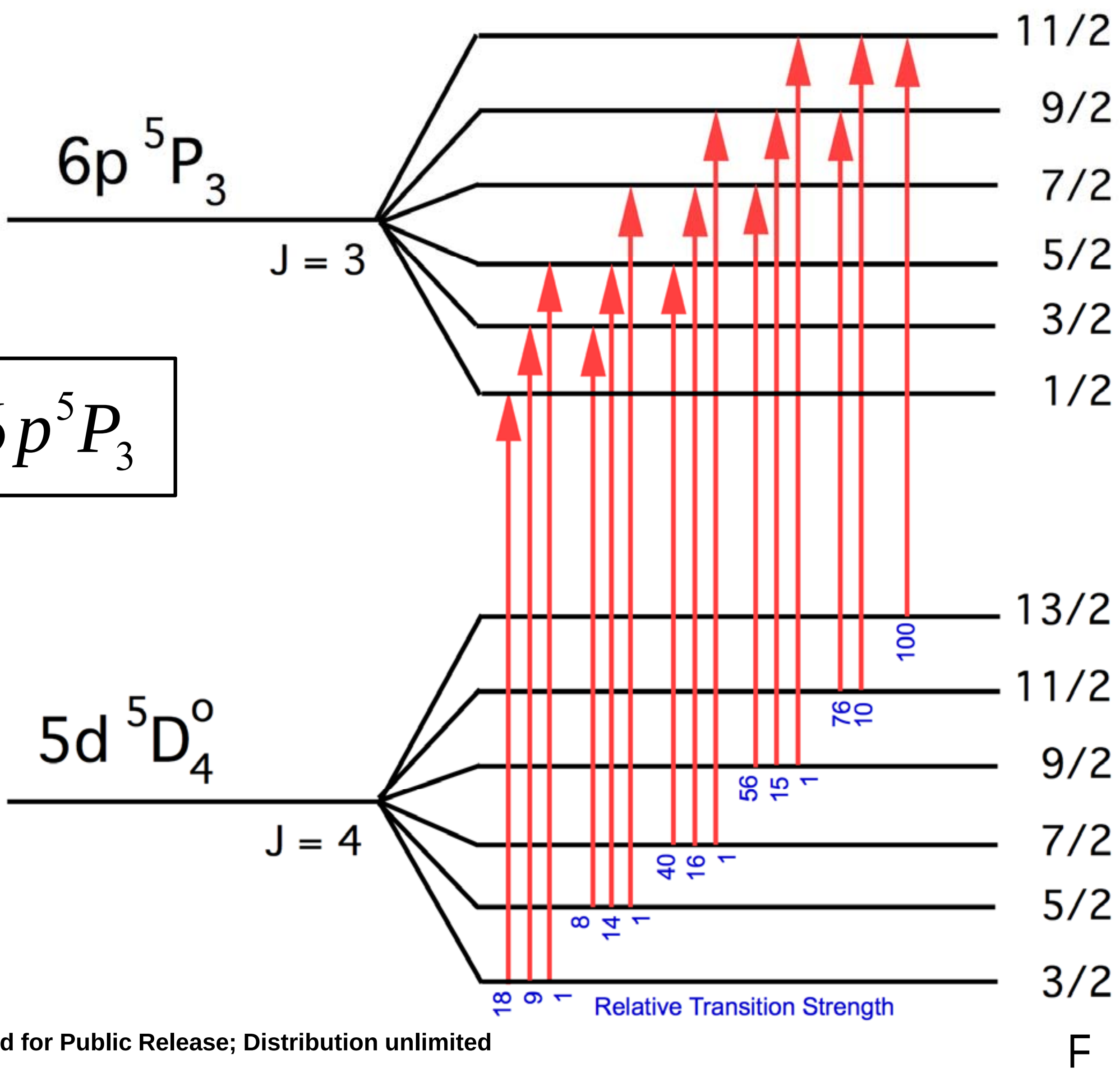
$$F \rightarrow F : S = \kappa\frac{[J(J+1)+F(F+1)+I(I+1)]^2(2F+1)}{F(F+1)}$$

$$F + 1 \rightarrow F : S = -\kappa\frac{(J+F+I-2)(J+F-I+1)(J-F+I)(J-F-I-1)}{(F+1)}$$

Hyperfine Spin Splitting:
I II Transition @ 695.9 nm Predictions

$$5d\,{}^5D_4^0 \rightarrow 6p\,{}^5P_3$$

I = 5/2



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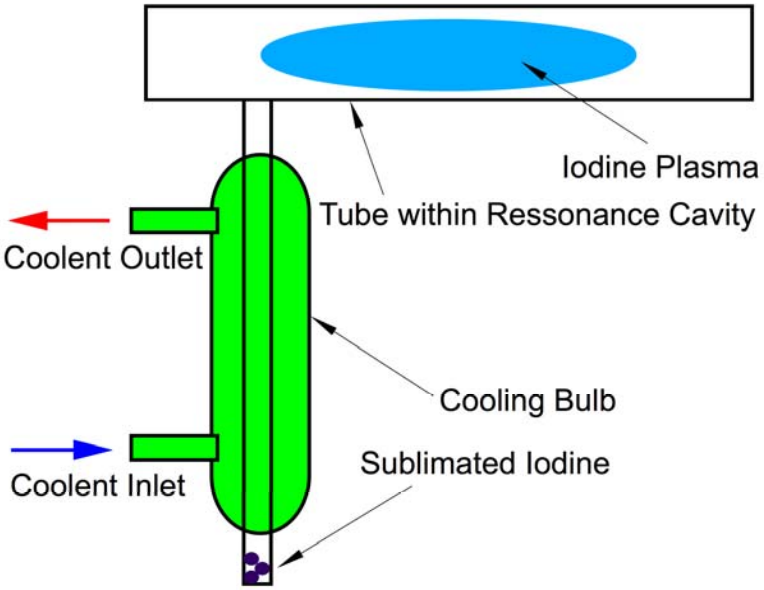
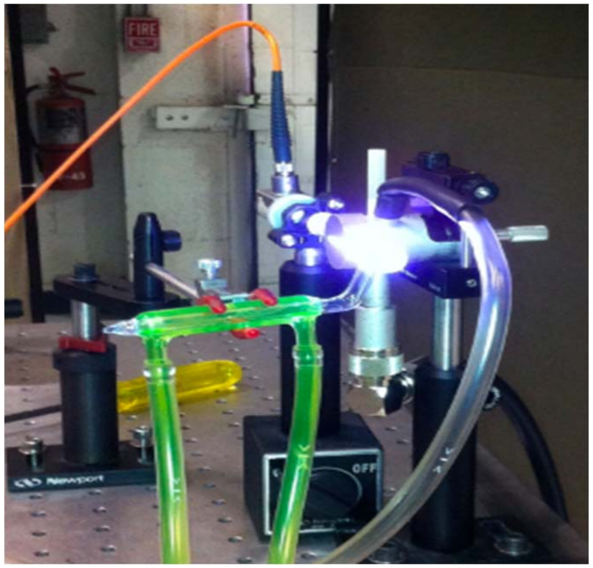
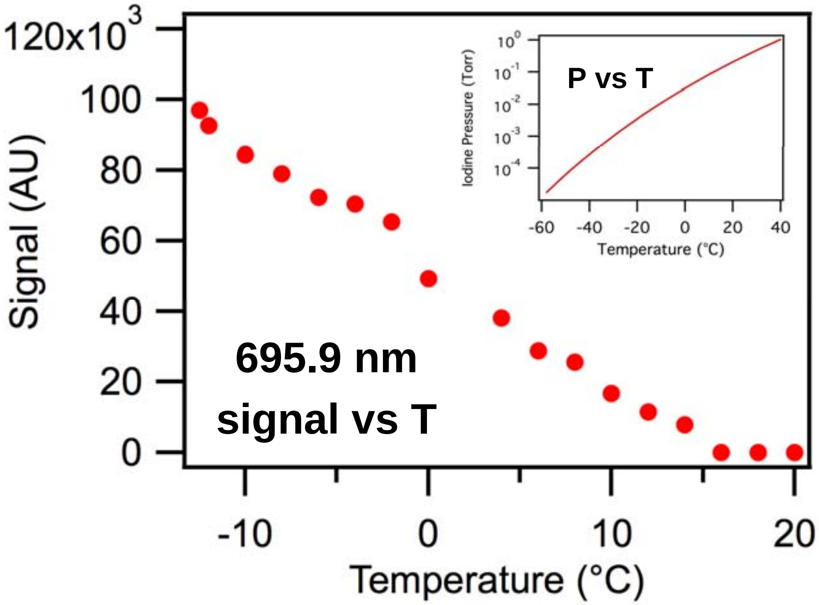
Tabletop Spectral Source







- **Tabletop spectral source**
  - **2.2 GHz resonant cavity (20-50 W)**
  - **Integral cooling bulb**
  - **Iodine density varied via temperature**
- **Initial results**
  - **-12° C minimum temperature**
  - **Reasonable signal strength**
- **Second lamp is under construction**

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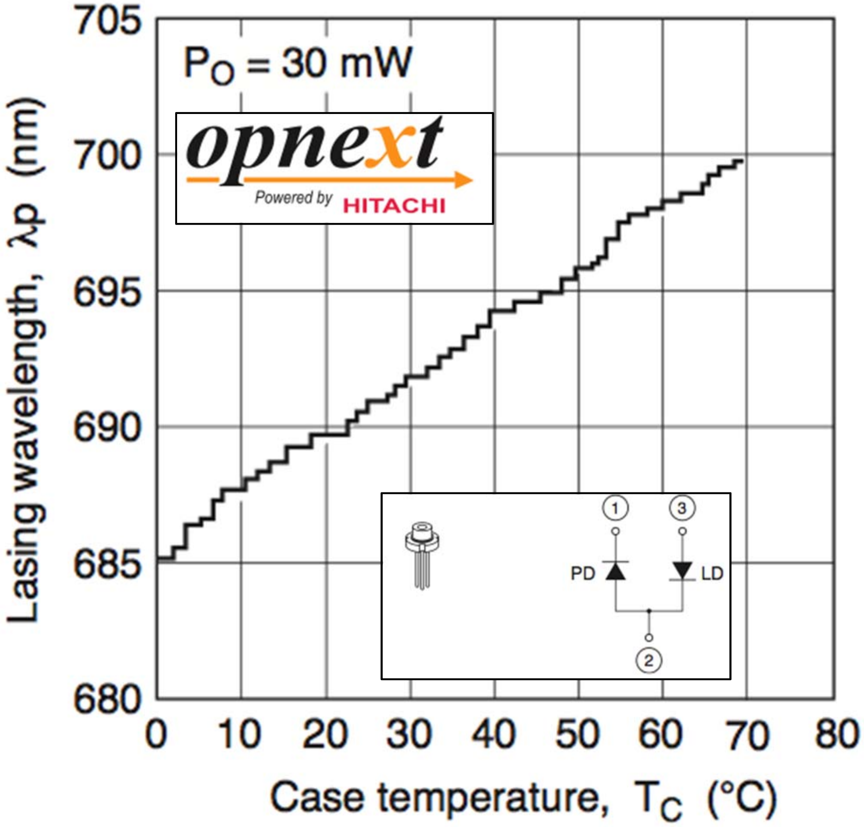
Laser Diode Selection



- Examining a number of alternatives
- Low cost COTS FP laser diode
  - Low cost ($50 for diode)
  - ~40 MHz line width
  - ~10 GHz scanning range
  - Wavelength selection is an issue
  - 30 mW power levels typical
  - Suitable for Doppler free spec.
- Commercial tunable lasers
  - Higher cost (~$30k)
  - 500 kHz line width
  - 100-200 GHz scanning range
  - Wavelength readily available
  - 2 mW power levels typical
- Analysis of alternatives underway

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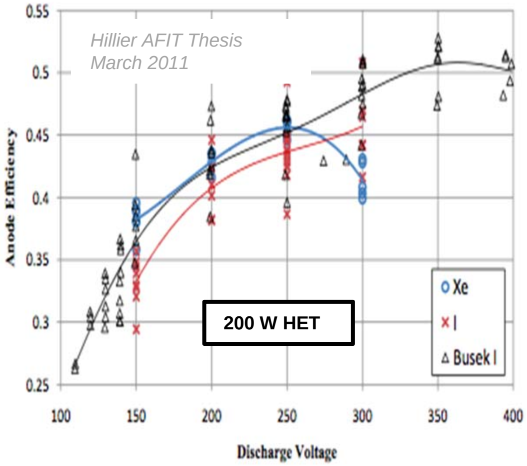
Summary and Conclusions and Future Work

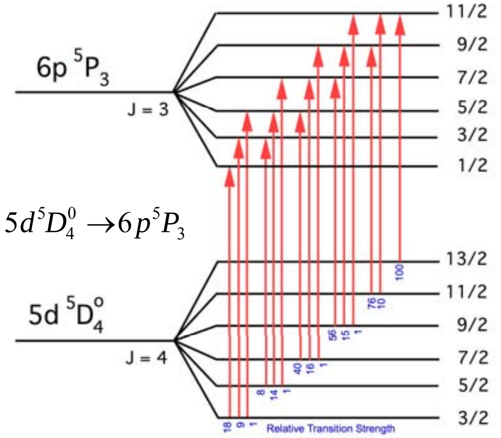
- **Iodine is a possible future HET and/or ion engine propellant**
  - Lower cost, relatively abundant, already demonstrated!
  - Similar, possibly improved performance compared to xenon
  - More complex propellant management system



Hillier AFIT Thesis
March 2011

200 W HET

- **Review of limited spectroscopic data**
  - Metastable lower state identified for maximum lower state populations
  - “Best” I II transition identified (@695.9 nm, $5d^5D_4^0 \rightarrow 6p^5P_3$)
  - Verified via HET emission 695.9 nm transition populating metastable lower state
  - Non-resonant fluorescence for signal collection (@516.2 nm, $6s^5S_2^0 \rightarrow 6p^5P_3$)
  - Verified via HET emission 516.2 nm transition for non-resonant signal collection
  - Determined number & relative magnitude of 15 hyperfine components, not separation…
- **Table top experimental apparatus**
  - Constructed two lamps
  - Second lamp (as presented) showed significant ion emission!
  - Laser selection in work.



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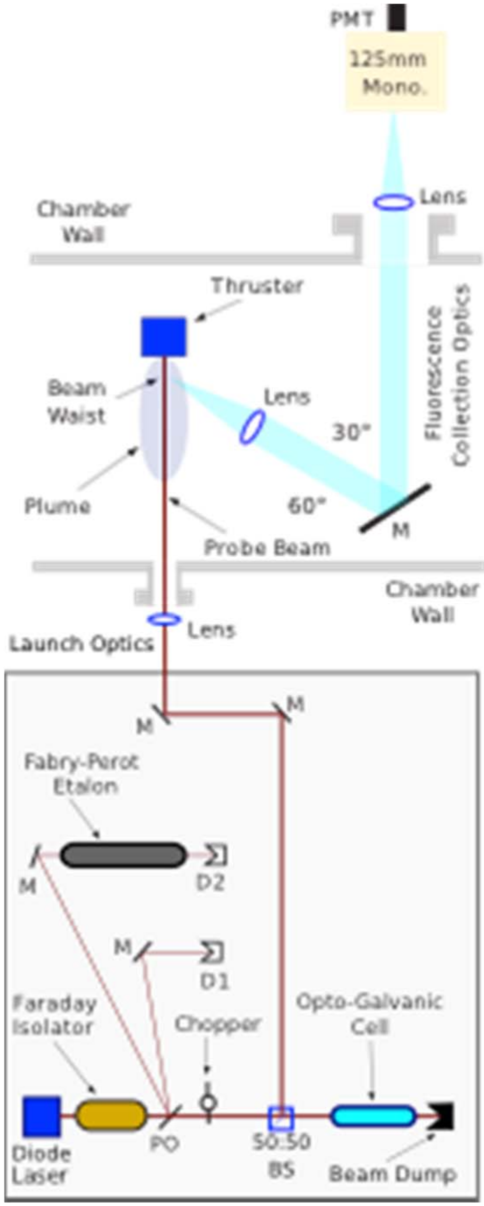
Future Work



- **Improved tabletop plasma source**
  - 250 mTorr helium fill for Penning effect for increased N_i
  - Improved cooling to minimize neutral quenching
- **Laser selection**
  - Choice 1 is 30+ mW tunable diode laser
    - Enables Doppler free analysis
    - Determination of hyperfine A & B constants
    - Only useful for table top experiments
    - Would (?) enable ion temperature
  - Choice 2 is ~2 mW laser tunable diode laser
    - Enables thruster measurements
    - Insufficient for detailed hyperfine analysis
    - Readily available
- **Eventual goal is measurement within HET**
- **Are other species of interest? (e.g. I, I_2, I_2^+)**

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