Development of a Fast Ion Beam Spectrometer for Molecular Ion Spectroscopy

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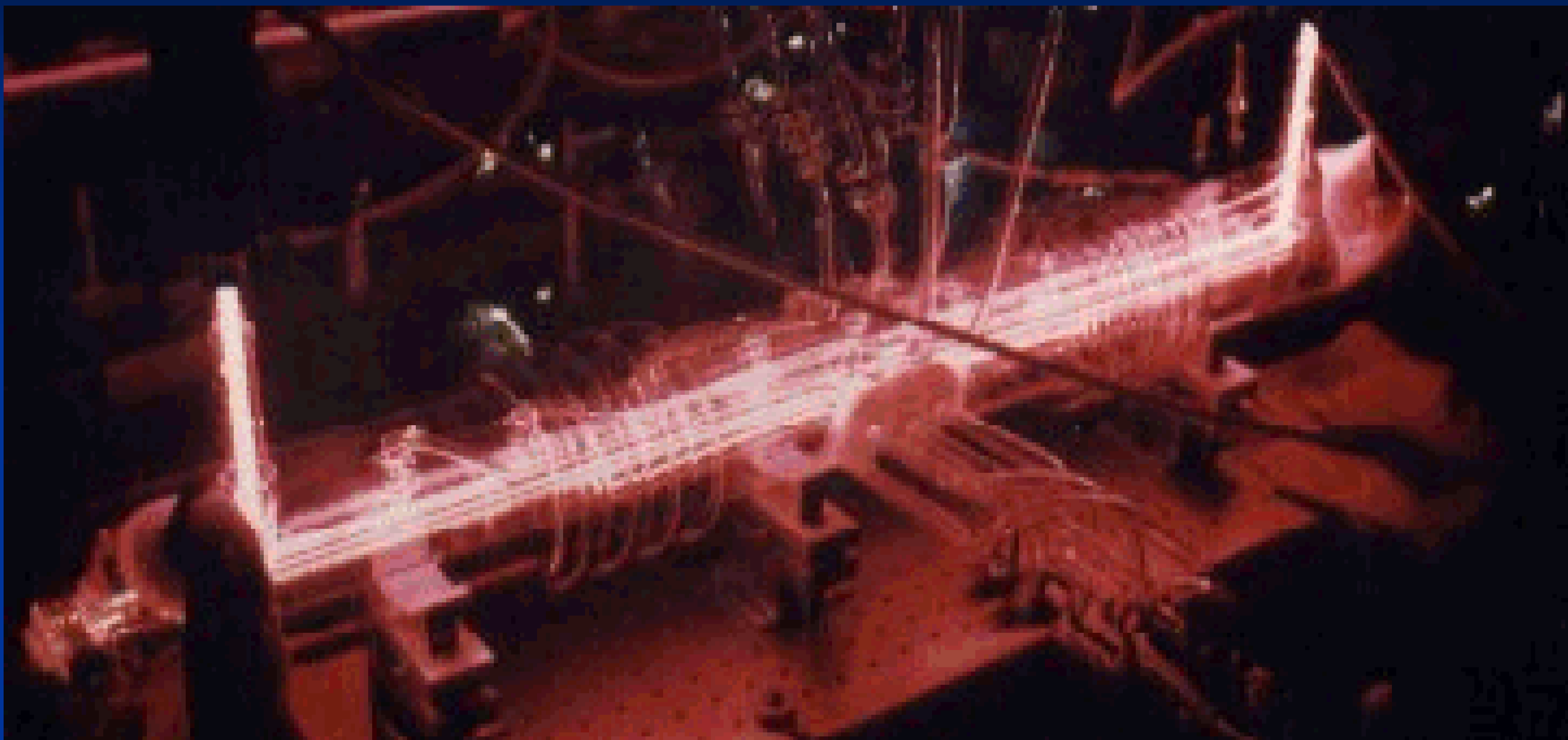
Molecular Ions

- Carbocations:
  - Involved in S_N1, aromatic substitutions, rearrangements
  - Low densities and temperatures (Astrochemistry) require accurate & precise spectra of many lines with assignments
  - Complex intra-molecular dynamics making detailed spectra where assignment is difficult
  - Many molecules & high temperature → complications
  - High resolution spectroscopy is the key
  - Ion production
  - Sensitive spectroscopy

Production of Ions - Plasmas



- 10^{12} cm^{-3}
- T 300 K - 1000 K
- [neutrals]/[ions] ~ (10^6)

http://fermi.uchicago.edu/photo/discharges/

Selectivity of Ions

- Velocity Modulation
  - Polarity modulation suppresses absorption by neutrals (Ions at frequency f, neutrals at 2f)
  - Opposite polarity ions travel different directions, inducing change in line shape based on polarity of ion.
  - Many ions in plasma → Overlapping Spectra

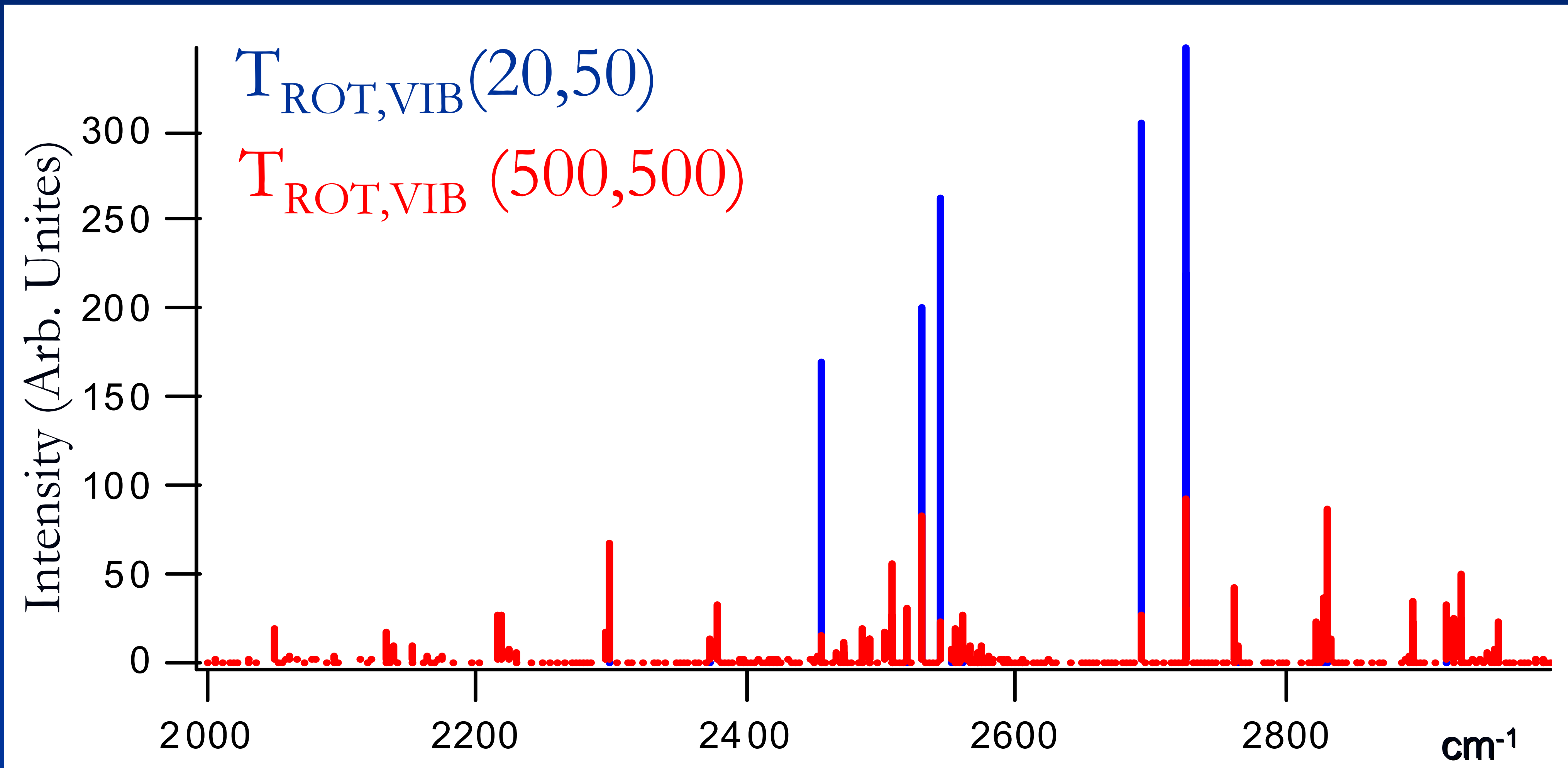
$$\Delta\nu \propto \frac{1}{\sqrt{M}}$$

  - Molecules have high rotation, vibrational and translation temperatures

Gudeman, Begemann, Pfaff, Saykally, *Phys. Rev. Lett.* **50** (1983), 727.

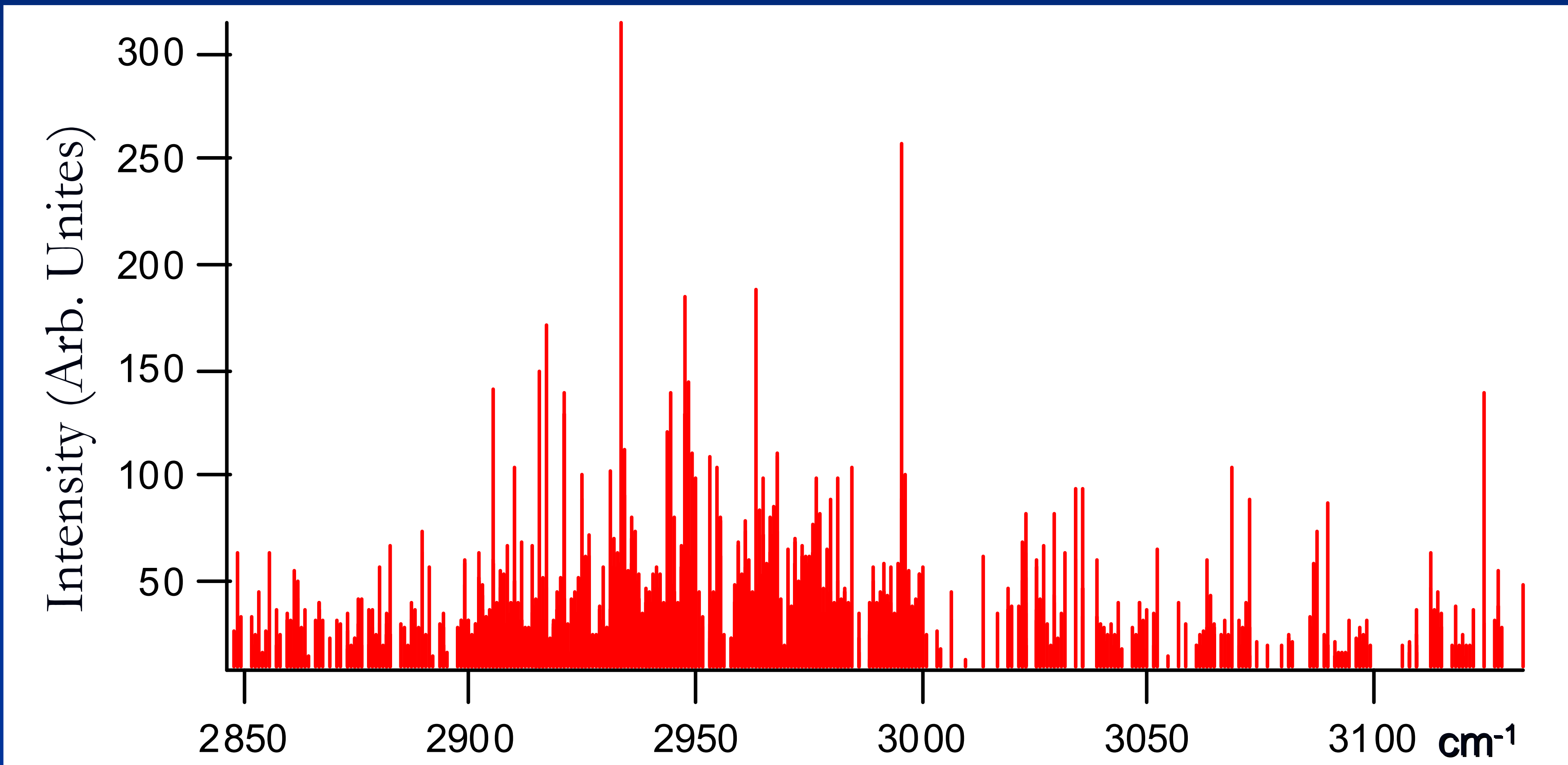
Stephenson & Saykally, *Chem. Rev.* **105** (2005), 3220.

Effect of Temperature on H_3^+



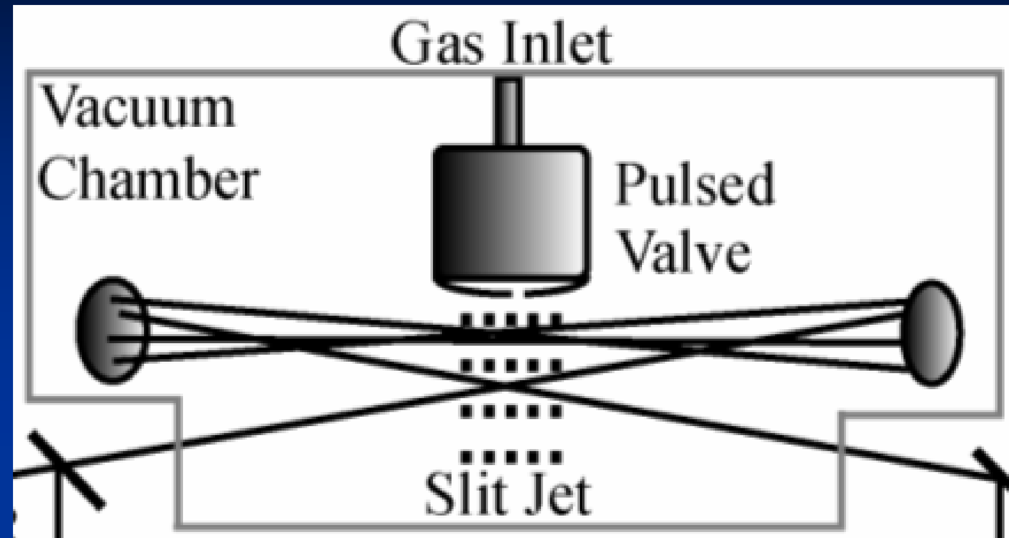
http://h3plus.uiuc.edu/criteval/calc.shtml

Oka's Congested CH_5^+ Spectrum



E. T. White, J. Tang, Takeshi Oka *Science* **284**, (1999) 135

Slit Expansions

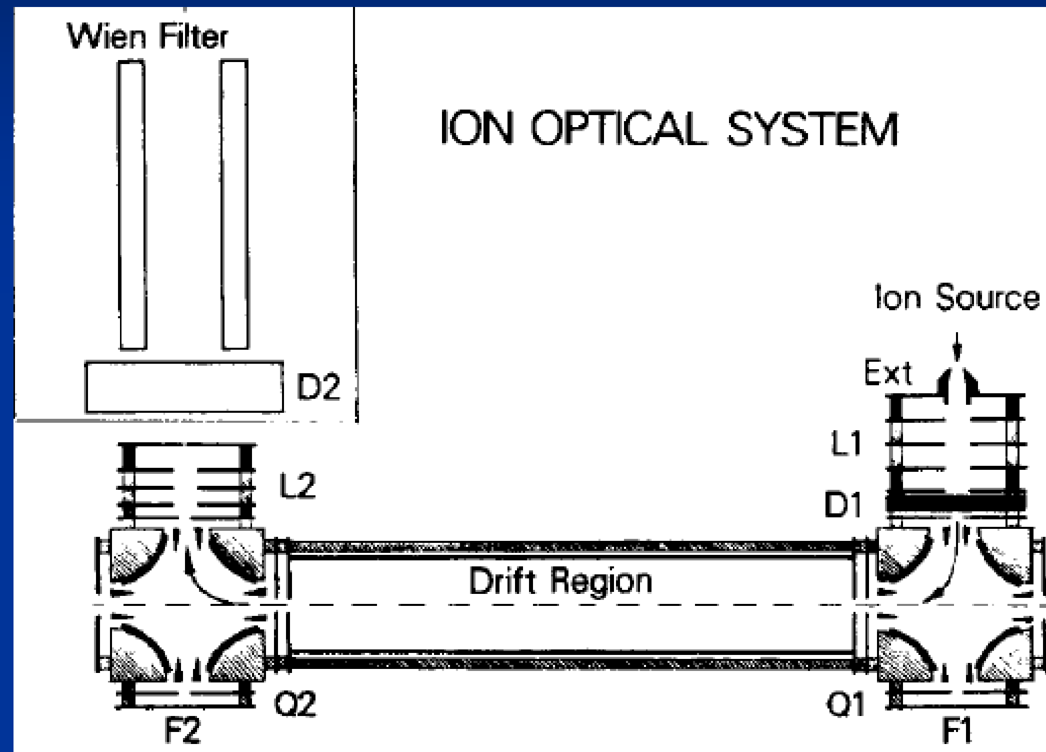


- Supersonic expansion slit source
  - Rot & Vib Cold
  - Sub-Doppler line widths: 120 MHz
- Direct absorption
- (White cell 64 cm.) 10^{-5} cm^{-1}
- Concentration modulation: Modulates plasma
- Ion/neutral discrimination: titration

Dong,. Uy, Davis, Child, Nesbitt, *J. Chem. Phys.* **122**, 2005 224301.

Direct Laser Absorption Spectroscopy in Fast Ion Beams (DLASFIB)

- Uncooled cold cathode DC w/ floated discharge source
- 20-40 MHz line width from kinematic compression
- Ion optics collimate; Electrostatic quadrupole turns
- Ion densities ~ 10^7 cm^{-3}
- Low finesse etalon
- Direct absorption (**10^{-7} cm^{-1}**)
- Color center laser
- Doppler splitting yields charge to mass ratio of each carrier



Coe,Owrutsky, Keim, Agman, Hovde, Saykally. J. Chem. Phys. **90**, (1989) 3893.

Improvements

Saykally

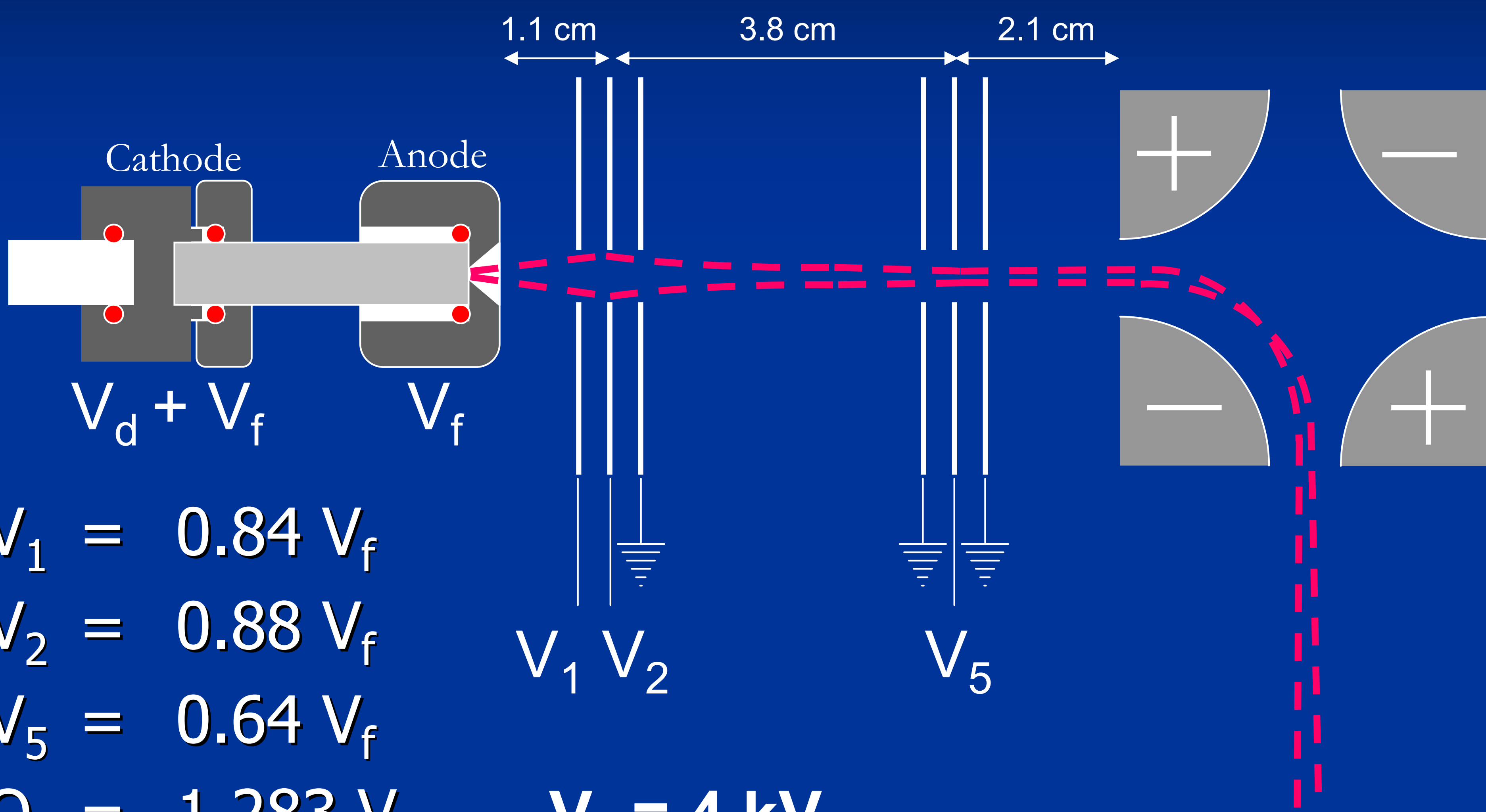
- Color center laser
- Etalon multi-pass
- Un-cooled cathode
- FIB kinematic comp.
- Wien filter MS

McCall

- DFG-PPLN
- Cavity ring-down
- Supersonic expansion
- FIB kinematic comp.
- ToF MS

	Reflectivity	Finesse	Round Trips	Pathlength single	Pathlength total
				cm	m
Saykally	0.98	155	25	15	3.7
McCall	0.9999	31414	5000	33	1649.9

Ion Optics & Quadrupole



$V_1 = 0.84\ V_f$

$V_2 = 0.88\ V_f$

$V_5 = 0.64\ V_f$

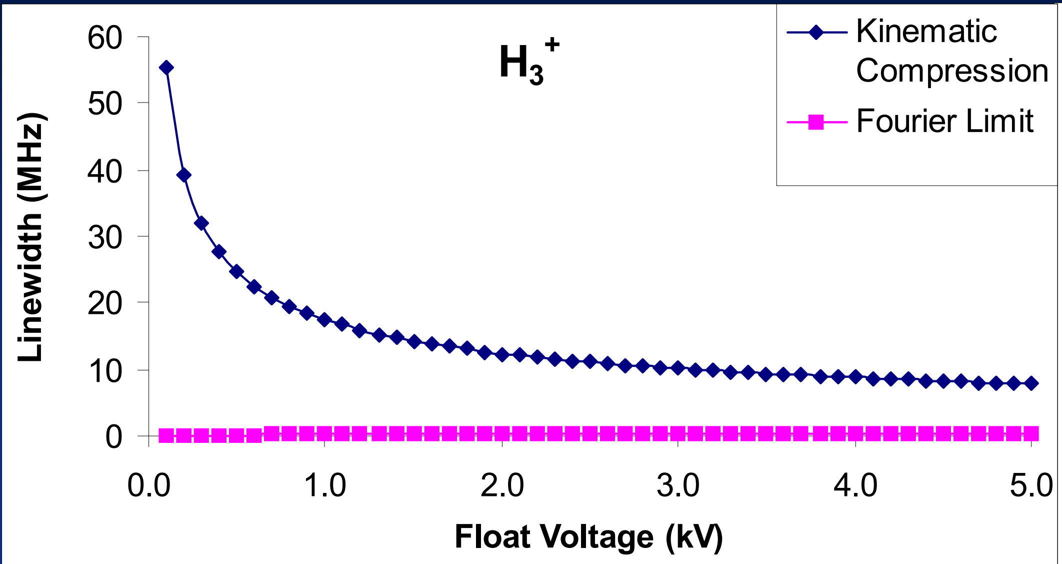
$Q_+ = 1.283\ V_f$

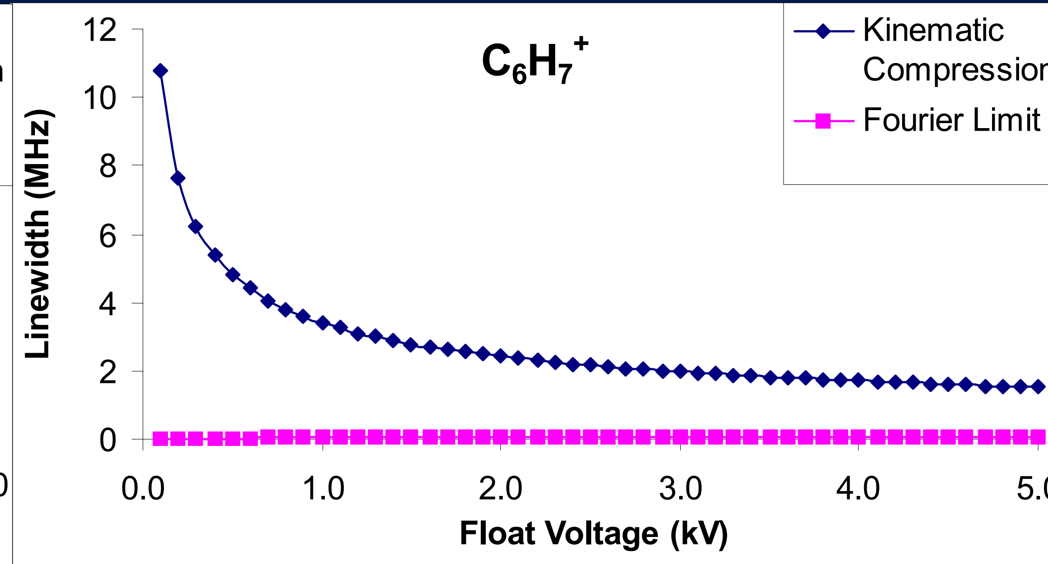
$Q_- = 1.425\ V_f$

V_f = 4 kV

V_d = 3.5 kV

Kinematic Compression





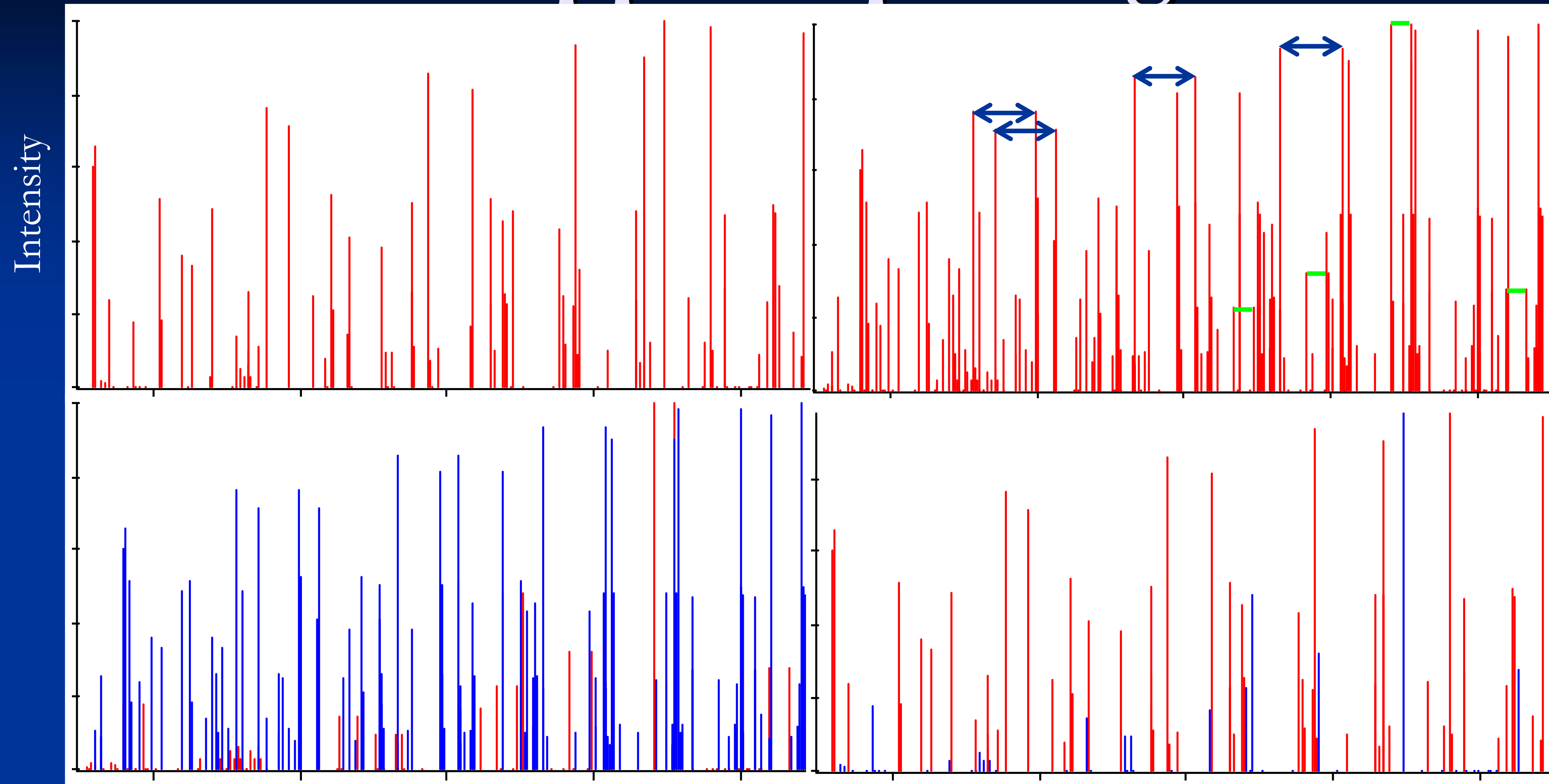
$$\Delta\nu_{Fourier} \approx \frac{1}{l2\pi}\sqrt{\frac{2qV_f}{M}}$$

$$\Delta\nu_{Kinematic} = \frac{2\nu_0}{c}\sqrt{\frac{2kT}{M}+\frac{2eV_f}{M}}$$

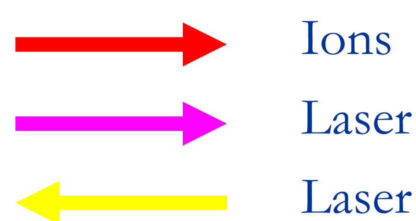
- $\Delta v/v_0$ becomes smaller with high V_{Float}
- Tighter line widths ➔ stronger absorption and higher resolution

S.L. Kaufman. Optics Communications 17 (3) 1976 309-312.

Doppler Splitting



Center Frequency ~ 2000 cm^{-1}				
Mass	V_{FLOAT}			
AMU	4000	3000	2000	1000
3.0	6.73	5.83	4.76	3.37
16.0	2.92	2.53	2.07	1.46
28.0	2.21	1.92	1.56	1.11
79.1	1.32	1.14	0.93	0.66

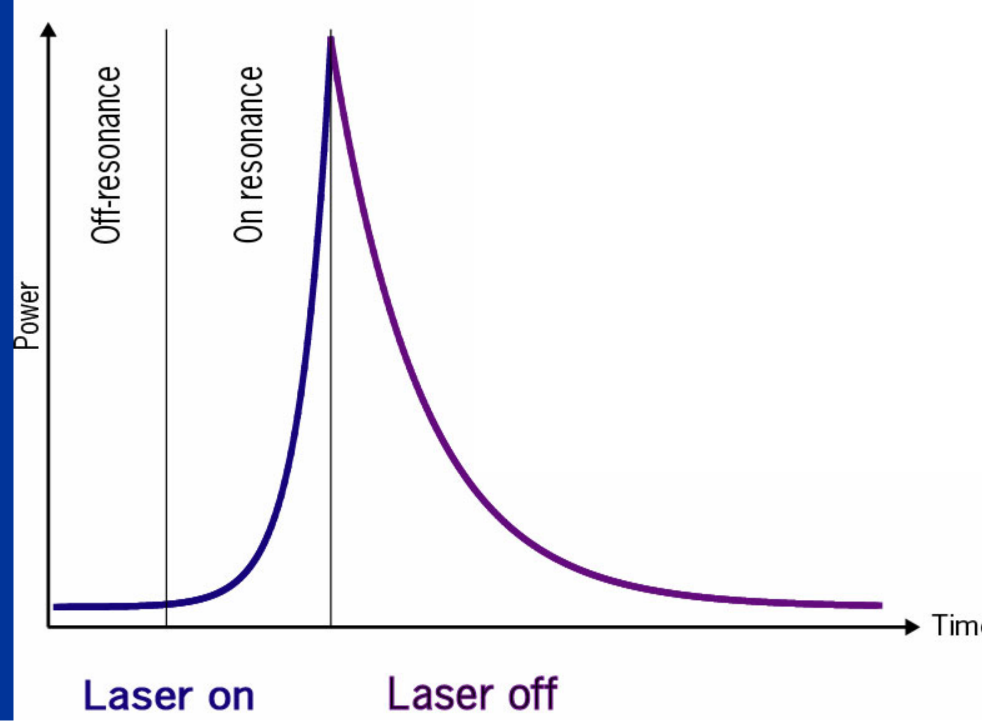


$$\nu_{eff} = \nu_1 \left[1 \mp \sqrt{\frac{2eV_f}{mc^2}} \right]$$

cw Cavity Ring-down Spectroscopy

- A high finesse cavity placed around ion drift region
- Laser light is coupled into the cavity
- Cavity is dithered in and out of resonance
- At threshold intensity the laser is switched off
- Characteristic time constant is measure of absorption
- Typical 10^{-9} cm^{-1}
- High Repetition 10^{-10} cm^{-1}
- NICE-OHMS 10^{-13} cm^{-1}

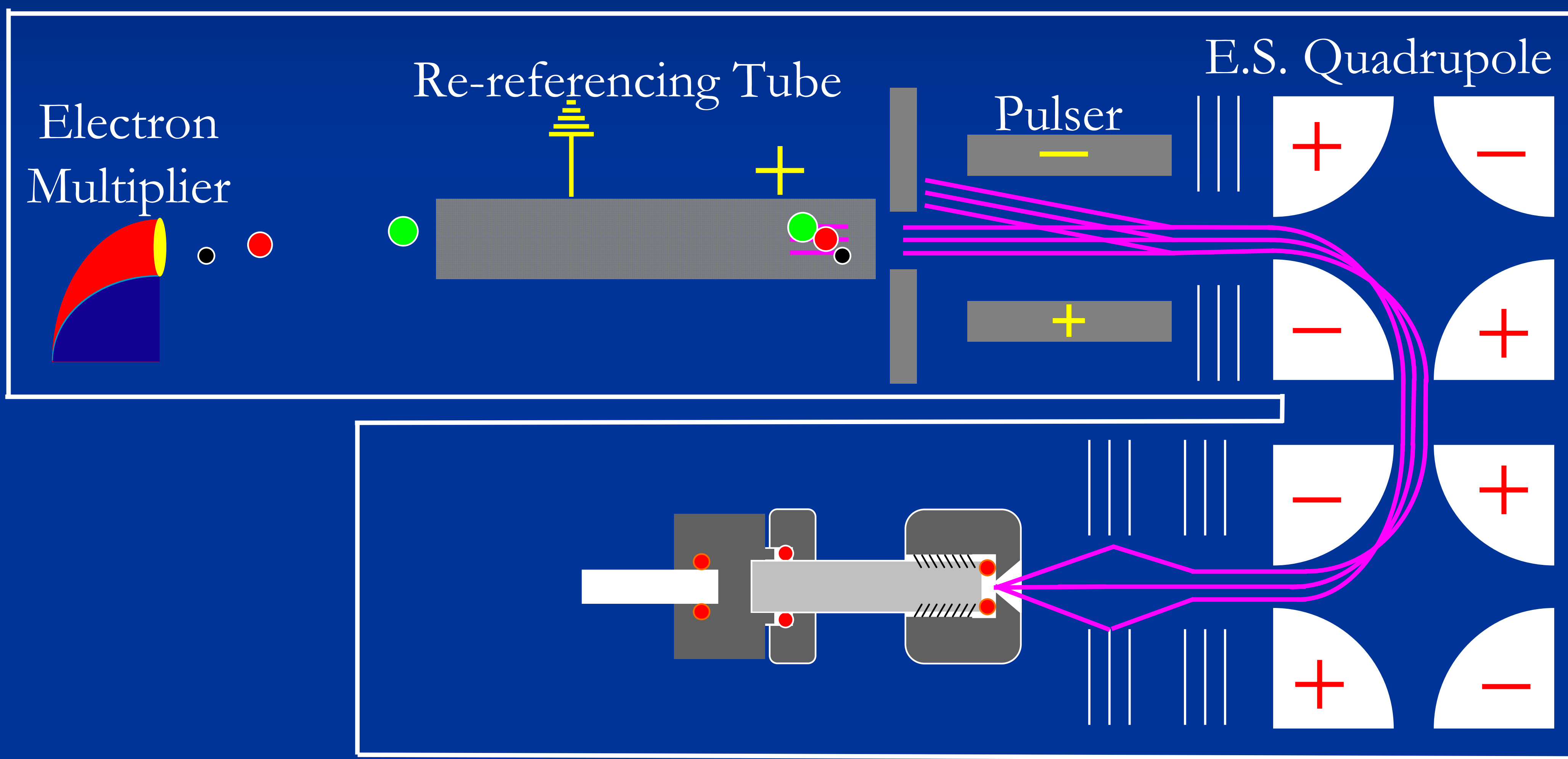
Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy



Spence et al. *Review of Scientific Instrumentation* **71** (2) **2000** 347-353

van L.eeuwen & Wilson JOSAB **21** (10) **2004** 1713-1721

ToF-MS


E.S. Quadrupole
Pulser
Re-referencing Tube
Electron
Multiplier

Conclusions

- Plasmas are useful sources for molecular ions, yet create ions with high T_{vib} and $T_{rot.}$
- Velocity modulation can effectively discriminate against neutrals, but cannot produce cool molecules.
- Slit jets utilize supersonic expansions to cool molecules formed in plasma discharges, but cannot spectroscopically discriminate against neutrals.
- DLASFIB provided a technique to perform spectroscopy while separating ions from neutrals. However, efficient tunable lasers and sensitive spectroscopy had yet to be developed.
- By coupling highly sensitive cavity ring-down, with a widely tunable DFG laser system we will produce simpler spectra of molecular ions.
- The following talk will discuss the development of our technique.