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 $\rightarrow$ complications
  - High resolution spectroscopy is the key
  - Ion production
  - Sensitive spectroscopy
Production of Ions - Plasmas

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

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 $\rightarrow$ Overlapping Spectra

\[ \Delta \nu \propto \frac{1}{\sqrt{M}} \]

- Molecules have high rotation, vibrational and translation temperatures


Effect of Temperature on $\text{H}_3^+$

$T_{\text{ROT,VIB}} (20,50)$

$T_{\text{ROT,VIB}} (500,500)$

http://h3plus.uiuc.edu/criteval/calc.shtml
Oka’s Congested CH$_5^+$ Spectrum

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

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 \( \sim 10^7 \text{ cm}^{-3} \)
- Low finesse etalon
- Direct absorption \( (10^{-7} \text{ cm}^{-1}) \)
- Color center laser
- Doppler splitting yields charge to mass ratio of each carrier

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

<table>
<thead>
<tr>
<th></th>
<th>Reflectivity</th>
<th>Finesse</th>
<th>Round Trips</th>
<th>Pathlength single</th>
<th>Pathlength total</th>
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<tbody>
<tr>
<td><strong>Saykally</strong></td>
<td>0.98</td>
<td>155</td>
<td>25</td>
<td>15</td>
<td>3.7</td>
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<td><strong>McCall</strong></td>
<td>0.9999</td>
<td>31414</td>
<td>5000</td>
<td>33</td>
<td>1649.9</td>
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</table>
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**
\[ \Delta v_{\text{Fourier}} \approx \frac{1}{l 2\pi} \sqrt{\frac{2qV_f}{M}} \]

\[ \Delta v_{\text{Kinematic}} = \frac{2v_0}{c} \sqrt{\frac{2kT}{M} + \frac{2eV_f}{M}} \]

- \( \Delta v/v_0 \) becomes smaller with high \( V_{\text{Float}} \)
- Tighter line widths \( \rightarrow \) stronger absorption and higher resolution

Doppler Splitting

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

Center Frequency ~ 2000 cm\(^{-1}\)

<table>
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<tr>
<th>Mass (AMU)</th>
<th>(V_{\text{FLOAT}})</th>
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<tbody>
<tr>
<td>3.0</td>
<td>6.73 5.83 4.76 3.37</td>
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<tr>
<td>16.0</td>
<td>2.92 2.53 2.07 1.46</td>
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<tr>
<td>28.0</td>
<td>2.21 1.92 1.56 1.11</td>
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<tr>
<td>79.1</td>
<td>1.32 1.14 0.93 0.66</td>
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</table>
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


van Leeuwen & Wilson *JOSAB* 21 (10) 2004 1713-1721
Conclusions

- Plasmas are useful sources for molecular ions, yet create ions with high $T_{\text{vib}}$ and $T_{\text{rot}}$.

- 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.