**Hydrogenic Plasmas in a Cold Hollow Cathode**

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### EXPERIMENT

**Hollow Cathode**
- 1.4 m copper cathode (1.5" OD) wrapped by ¾" copper tube for cooling with a variety of media  
- A water-cooled anode is located at the mid-point of the cathode  
- Discharge is guided by a quartz tube to the interior of the cathode  
- Sealed with BaF₂ windows at Brewster's Angle  
- Supports 1-2 sample gasses

**Difference Frequency Laser**
- Combine tunable Ti:Sapphire laser and fixed Nd:YAG laser in periodically poled lithium niobate (PPLN) crystal  
- Tunable between 2.8-4.8 µm

**White Cell**
- Consists of three, 2 m radius of curvature gold mirrors  
- Reflectance >95% between 630 nm and 10 µm  
- White cell provides 16+ m path length  
- Output detected using DC indium-antimonide detector

### MOTIVATION

H₃⁺ is a key constituent for much of the gas-phase chemistry occurring in the interstellar medium (ISM). The ortho- and para-nuclear spin modifications of both H₂ and H₃⁺ are essentially separate chemical species, and their distribution is the source of two great astrochemical mysteries.

1) Why is the "excitation temperature" of para-H₂ and ortho-H₃⁺ in diffuse clouds 20-40 K lower than the temperature determined by other methods?  
2) How does H₃⁺, formed with an ortho:para ratio of 3:1, thermalize to nearly all para-H₃⁺ in dense molecular clouds?

The answers to these questions are hidden in the dynamics of the reaction

\[
H_3^+ + H_2 \rightarrow H_2 + H_3^+ 
\]

which can change the spin modification of both molecules. Indeed, an understanding of this simple and most common bimolecular reaction in the universe is of fundamental importance.

### THEORY

A reaction between H₃⁺ and H₂ can follow one of two pathways: proton hop or hydrogen exchange.

- **Hydrogen Exchange**
  - Spin selection rules dictate only para-H₃⁺ will initially form in a discharge of pure para-H₂ (Quack Met Phys, 34, 417)
  - In pure para-H₂, para-H₃⁺ can be converted to ortho-H₂⁺ only by the exchange reaction. A term used to compare these pathways is \( \alpha = \frac{k_{ortho}}{k_{exchange}} \). Hollow cathode measurements show \( \alpha \approx 2.4 \) at 300 K (Raymond & Gorti, 1999, ApJ, 511, 149)
  - Starting with highly enriched para-H₂, any ortho-H₂⁺ present is therefore a direct measure of proton exchange.
  - In this manner \( \alpha \) can be inferred.

- **Proton Hop**

### TEMPERATURE MEASUREMENTS

\[
\frac{n_x}{n_y} = \frac{(g_x g_I)}{(g_y g_J)} \exp \left( \frac{-\Delta E}{k_B T} \right)
\]

- Measured \( T_{rotation} \), \( T_{kinetic} \), and \( T_{rotational} \)
  - Temperature was \( \approx 150 \) K
  - We are still analyzing \( T_{rotational} \), which seems to be cooler than expected

### H₃⁺ + H₂ → H₂ + H₃⁺ Reaction Dynamics

- **Para-H₃⁺ and H₂ Fractions**
  - The para-H₃⁺ fraction \( (p_x) \) is dependent on the para-H₂ fraction \( (p_y) \) and temperature  
  - \( \alpha \) is also dependent on temperature; \( k_{exchange} \) dominates at low temperatures

- **Ratios of Ground State H₃⁺ and H₂**
  - Astronomical observations correlate with laboratory measurements
  - This correlation is evidence that H₃⁺ + H₂ → H₂ + H₃⁺ could be driving both the para-H₃⁺ and para-H₂ fractions in the ISM

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*Images and data from various sources, used for illustrative purposes.*