Hydrogenic Plasmas in a Cold Hollow Cathode

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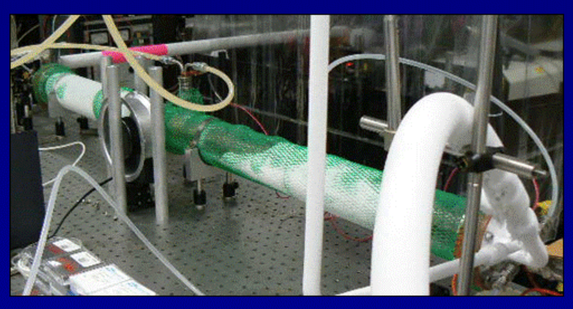
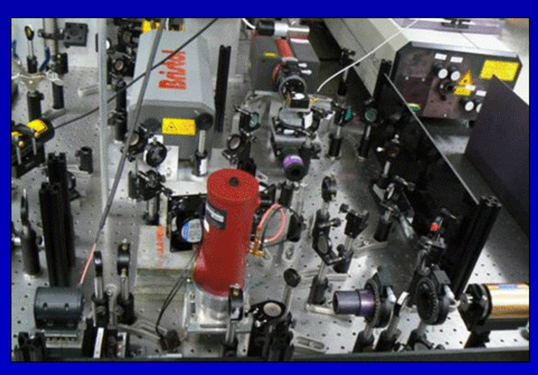
Advancing Chemical Understanding through Astronomical Observations

EXPERIMENT



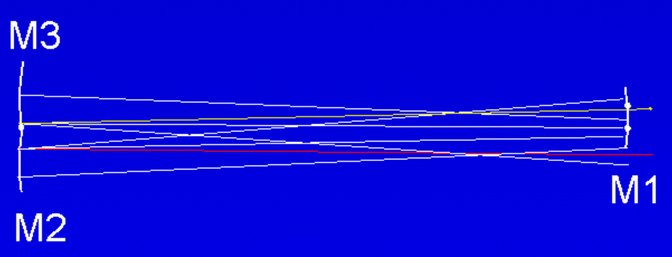
Hollow Cathode

- 1.4 m copper cathode (1.5″ OD) wrapped by ¼″ 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 BaF_2 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

H_3^+ 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 H_2 and H_3^+ are essentially separate chemical species, and their distribution is the source of two great astrochemical mysteries.

1) Why is the "excitation temperature" of *para*-H_3^+ and *ortho*-H_3^+ in diffuse clouds 20-40 K lower than the temperature determined by other methods?
2) How does H_2, formed with an *ortho:para* ratio of 3:1, thermalize to nearly all *para*-H_2 in dense molecular clouds?

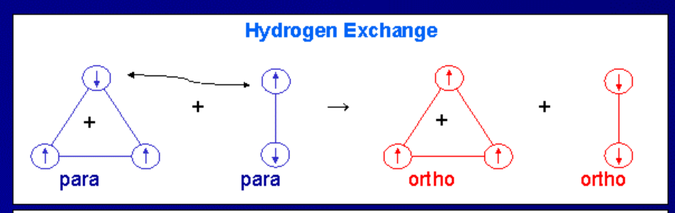
The answers to these questions are hidden in the dynamics of the reaction

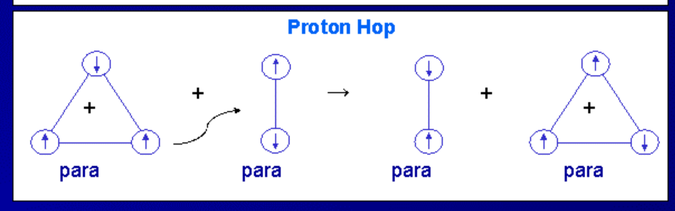
$$H_3^+ + H_2 \rightarrow H_2 + H_3^+$$

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

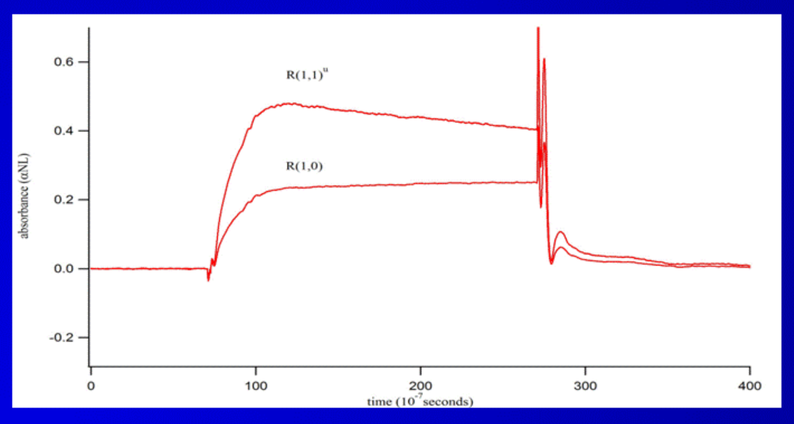
A reaction between H_3^+ and H_2 can follow one of two pathways: proton hop or hydrogen exchange.

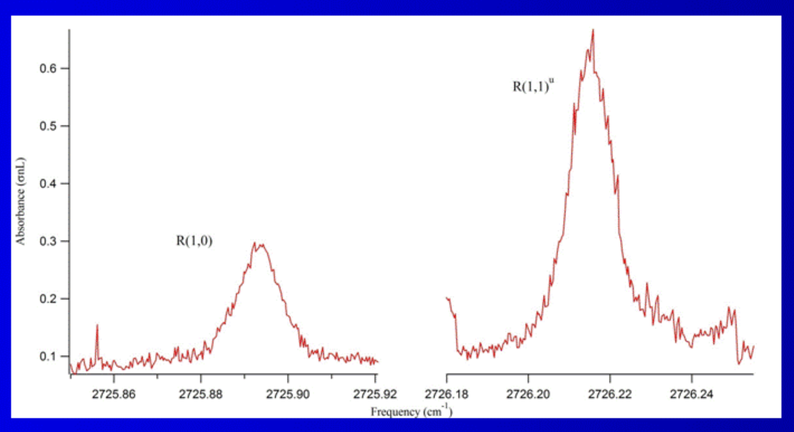




- Spin selection rules dictate only *para*-H_3^+ will initially form in a discharge of pure *para*-H_2 (Quack, Mol. Phys., 34, 477)
- In pure *para*-H_2, *para*-H_3^+ can be converted to *ortho*-H_3^+ only by the exchange reaction. A term used to compare these pathways is $\alpha = k_{hop}/k_{exchange}$. Hollow cathode measurements show $\alpha \sim 2.4$ at 300 K. (Cordonnier et al., J. Chem Phys, 113, 3181.)
- Starting with highly enriched *para*-H_2, any *ortho*-H_3^+ present is therefore a direct measure of proton exchange.
- In this manner α can be inferred.

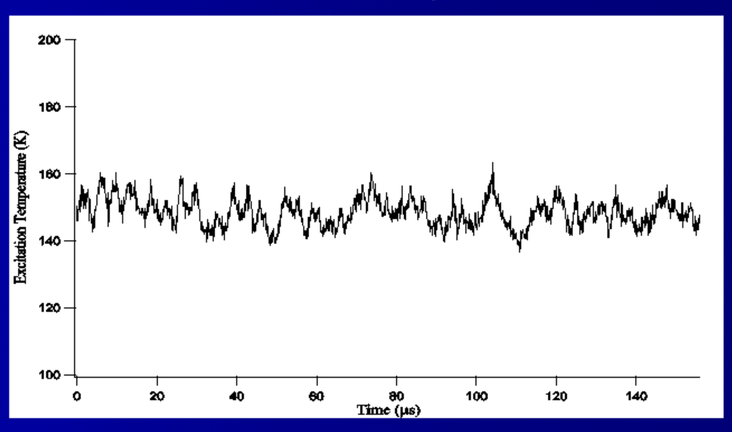
TEMPERATURE MEASUREMENTS



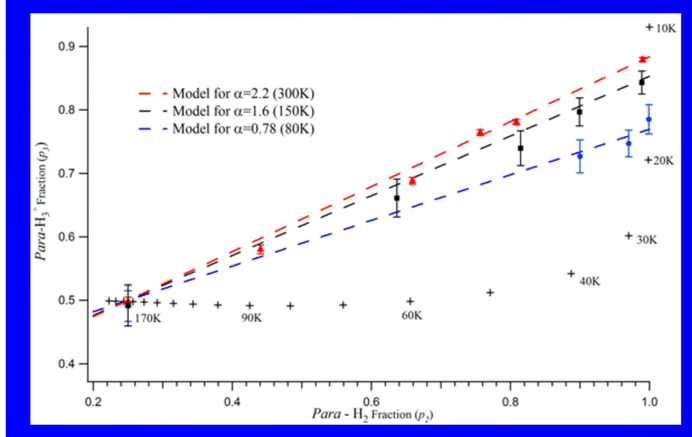


$$\frac{n_x}{n_y} = \frac{(g_J g_I)_x}{(g_J g_I)_y} \exp\left(\frac{-\Delta E}{k_b T}\right)$$

- Measured $T_{excitation}$ $T_{kinetic}$ and $T_{rotational}$
- Temperature was ~150 K
- We are still analyzing $T_{rotational}$ which seems to be cooler than expected

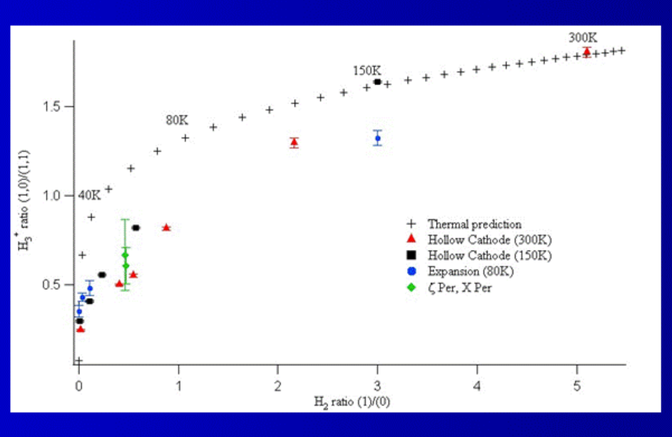


$H_3^+ + H_2 \rightarrow H_2 + H_3^+$ Reaction Dynamics



Para- H_3^+ and H_2 Fractions

- The *para*-H_3^+ fraction (p_3) is dependent on the *para*-H_2 fraction (p_2) and temperature
- α is also dependent on temperature; $k_{exchange}$ dominates at low temperatures



Ratios of Ground State H_3^+ and H_2

- Astronomical observations correlate with laboratory measurements
- This correlation is evidence that $H_3^+ + H_2 \rightarrow H_2 + H_3^+$ could be driving both the *para*-H_3^+ and *para*-H_2 fractions in the ISM

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