Nuclear Spin Effects in the Reactions of H_3^+ with H_2 and Electrons

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

Motivation

H_3^+ is the simplest polyatomic molecule. It is widely used as a benchmark for theoretical calculations of molecular spectroscopy and reaction dynamics, and also plays a pivotal role as the cornerstone of interstellar chemistry.

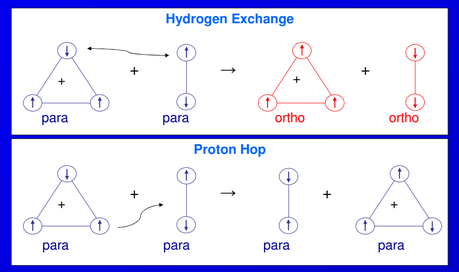
In Urbana, we have investigated the proton hop/ exchange reaction

$$H_3^+ + H_2 \rightarrow H_5^+ \rightarrow H_2 + H_3^+$$

for the first time at low temperatures. This reaction is the simplest bimolecular reaction involving a polyatomic, and is also the most common bimolecular reaction in the universe. Our experiments have revealed the branching ratio between proton hop and exchange, and may explain the observed ortho/para ratio of H_3^+ in diffuse interstellar clouds.

Theory

Reactions between H_3^+ and H_2 can proceed via two pathways: proton hop or hydrogen exchange.



Nuclear spin selection rules have an important influence on the branching ratio $\alpha = k_{hop}/k_{exchange}$. For example: in a discharge of pure p-H_2, the selection rules dictate that o-H_3^+ can only be formed via the exchange pathway. Taking the selection rules and applying them to a steady-state hydrogen plasma, we find for the p-H_3^+ fraction

$$p_3 = \frac{\alpha + 2\alpha\, p_2 + 1}{3\alpha + 2}$$

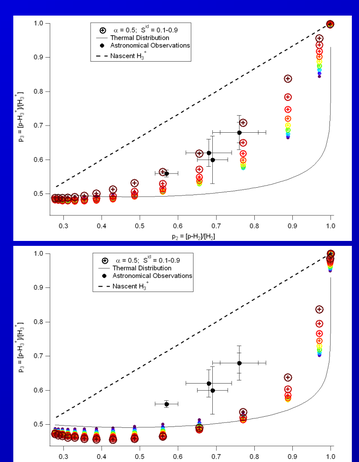
Steady State Modeling

Using the *para*-H_3^+ formation and destruction reaction rates, we can predict the *para*-H_3^+ fraction (p_3) formed in a plasma of a certain *para*-H_2 fraction (p_2). We use the microcanonical statistical model of Park and Light [6] to calculate k_{xxxx} rate coefficients, where the subscripts refer to the nuclear spin configurations of the (H_3^+, H_2) reactant and product pairs.

$$\begin{aligned}\frac{d}{dt}[p\text{-}H_3^+] &= k_1\left(\tfrac{2}{3}[o\text{-}H_2] + [p\text{-}H_2]\right)[p\text{-}H_2^+] + k_1\left(\tfrac{1}{3}[o\text{-}H_2] + \tfrac{2}{3}[p\text{-}H_2]\right)[o\text{-}H_2^+] \\ &+ \left\{\left(k_{oopp} + k_{oopo}\right)[o\text{-}H_2] + \left(k_{oppp} + k_{oppo}\right)[p\text{-}H_2]\right\}[o\text{-}H_3^+] \\ &- \left\{\left(k_{poop} + k_{pooo}\right)[o\text{-}H_2] + \left(k_{ppop} + k_{ppoo}\right)[p\text{-}H_2]\right\}[p\text{-}H_3^+] \\ &- k_{r(para)}[e_r^-][p\text{-}H_3^+],\end{aligned}$$

Line 1: *p*-H_3^+ formation. Line 2: *o*-$H_3^+ + H_2 \rightarrow$ *p*-$H_3^+ + H_2$.

Line 3: *o*-$H_3^+ + H_2 \rightarrow$ *p*-$H_3^+ + H_2$. Line 4: *p*-H_3^+ destruction via electron recombination



The best agreement between the modeling and diffuse cloud observations comes when S^{id} is 0.9 (corresponding to a "reactive" $H_3^+ + H_2$ rate coefficient of 1.5×10^{-10} cm^3 s^{-1}), and the *ortho* and *para* H_3^+ electron recombination rate coefficients are held equal at 2.0×10^{-7} cm^3 s^{-1} (upper left).

However, there is theoretical [1] and experimental [2] evidence that the electron recombination rate for *para*-H_3^+ is faster than that of *ortho*-H_3^+. Using the theoretical rate coefficients in [1], the p_3 curve shifts downward, as expected for the higher *p*-H_3^+ destruction rate. This curve cannot be brought into agreement with the observations even with $S^{id} = 1$. Note that all of this is insensitive to the value of α used. These efforts highlight the need for more conclusive experimental measurements of state-selective recombination rates to validate or invalidate this model.

[1] Fonseca dos Santos et al, JCP 127, 124309 (2007)

[2] Kreckel et at., PRA, accepted

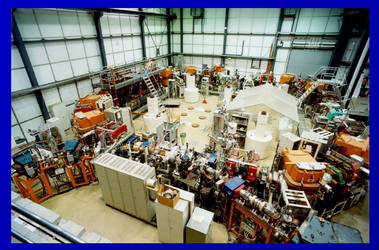
Dissociative Recombination (DR) of H_3^+ at the TSR storage ring

Motivation

The dissociative electron recombination

$H_3^+ + e \rightarrow H_2 + H$ or $H + H + H$

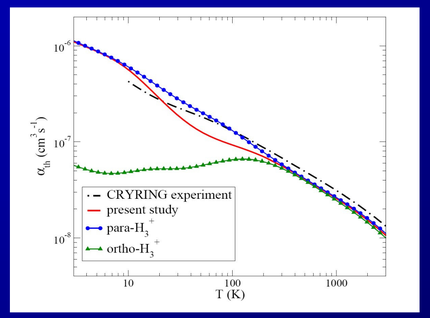
is the dominant destruction mechanism for H_3^+ in diffuse interstellar clouds. A strong dependence of the DR rate on nuclear spin might influence the para-H_3^+ fraction observed in interstellar clouds. The Storage ring technique allows for high-resolution DR measurements.



TSR storage ring / MPI-K Heidelberg

Theory

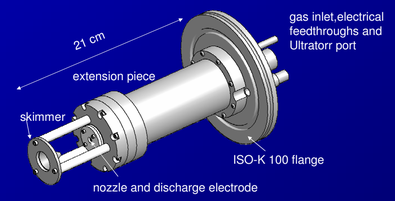
State-of-the-art theoretical calculations show a strong nuclear spin effect at low temperatures. The predicted rate coefficient is more than an order of magnitude faster for para-H_3^+ than for o-H_3^+ at 10K.



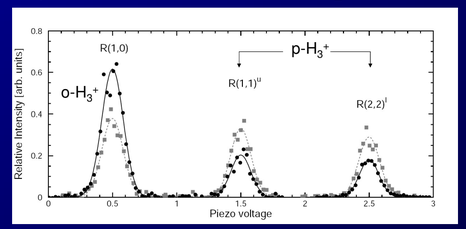
Calculated DR rate coefficient

Fonseca dos Santos et al, JCP 127, 124309 (2007)

Measurement

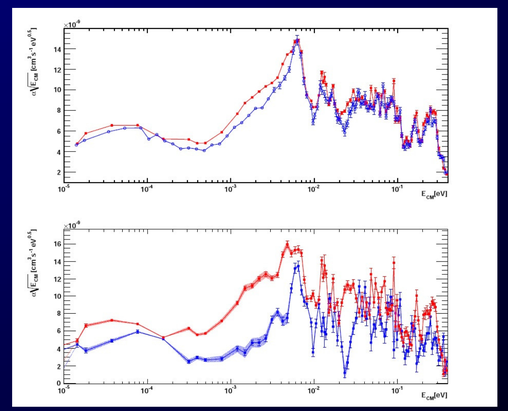


We used a supersonic ion source characterized by cavity-ringdown to produce H_3^+ ions for a DR measurement at the TSR storage ring. When used with 1:5 p-H_2:Ar precursor gas, we measure a p-H_3^+ fraction of 70.8% as compared to 47.9% with 1:5 n-H_2:Ar.



Cavity ringdown spectra recorded with n-H_2:Ar (black) and p-H_2:Ar (grey)

Comparison of the low-energy region of the H_3^+ DR rate coefficient measured with the expansion source with 1:5 n-H_2: Ar (blue) and 1:5 p-H_2: Ar (red) mixtures, respectively. The lower panel shows the extrapolated rate coefficients for p-H_3^+ (red) and o-H_3^+ (blue).



Nuclear spin and the low energy DR rate coefficient of H_3^+