

Communications: Development and characterization of a source of rotationally cold, enriched para-H₃⁺

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In an effort to develop a source of H₃⁺ that is almost entirely in a single quantum state ($J=K=1$), we have successfully generated a plasma that is enriched to $\sim 83\%$ in para-H₃⁺ at a rotational temperature of 80 K. This enrichment is a result of the nuclear spin selection rules at work in hydrogenic plasmas, which dictate that only para-H₃⁺ will form from para-H₂, and that para-H₃⁺ can be converted to ortho-H₃⁺ by subsequent reaction with H₂. This is the first experimental study in which the H₂ and H₃⁺ nuclear spin selection rules have been observed at cold temperatures. The ions were produced from a pulsed solenoid valve source, cooled by supersonic expansion, and interrogated via continuous-wave cavity ringdown spectroscopy. © 2010 American Institute of Physics. [doi:10.1063/1.3322827]

In 1911, Thomson¹ made the first experimental observation of the simplest polyatomic molecular ion, H₃⁺. Within 20 years, the existence of two species of molecular hydrogen, defined by the intrinsic spins of their protons, was predicted by Heisenberg and Hund.^{2,3} Shortly thereafter, Bonhoeffer and Harteck⁴ were able to experimentally prepare parahydrogen, in which the nuclear spins are antisymmetrically combined ($I=0$).

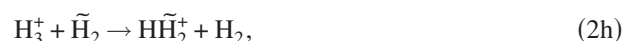
Hogness and Lunn⁵ discovered that H₃⁺ is the dominant species in hydrogenic plasmas, formed by



(exothermicity of ~ 1.7 eV and Langevin rate constant, $k_L \sim 10^{-9}$ cm³ s⁻¹).⁶ The relationship between the ortho and para spin modifications of molecular hydrogen and the ortho and para-H₃⁺ products, however, was not studied for another 50 years. New insight was gained when spin selection rules were derived by Quack using group theoretical methods,⁷ and later (using an angular momentum formalism) by Oka,⁸ for reaction (1) and for the reaction



Reaction (2) occurs in one out of three ways: identity (2i), proton hop (2h), or hydrogen exchange (2e),



Here, the hydrogens originally in the H₂ reactant are designated as $\tilde{\text{H}}$ in order to illustrate the differences between the three reactions.

As discussed by Cordonnier *et al.*,⁹ each of these pathways must obey strict selection rules imposed by the conservation of nuclear spin angular momentum. The effects of these selection rules have been experimentally observed by Uy *et al.*¹⁰ and Cordonnier *et al.*⁹ in hot (300–500 K) plasmas. In addition, Gerlich¹¹ studied the closely related D₃⁺ and H₂ system at much colder temperatures.

The selection rules for reaction (1) dictate that only para-H₃⁺ will form from pure para-H₂. However, in a hydrogenic plasma (where H₂ is several orders of magnitude more abundant than H₃⁺), reaction (2) will occur immediately following the formation of H₃⁺ and will affect its ortho:para ratio. This process has been considered in detail by Cordonnier *et al.*;⁹ their Table IV presents the nuclear spin branching ratios for this reaction. The identity reaction (2i) clearly has no effect on the H₃⁺ nuclear spin modification. If para-H₃⁺ combines with para-H₂ in the proton hop reaction (2h), the product H₃⁺ also emerges without spin conversion. The exchange reaction (2e) is the only mechanism that converts para-H₃⁺ to ortho-H₃⁺ in pure para-H₂. If ortho-H₂ is present, then para-H₃⁺ can also be converted to ortho-H₃⁺ via reaction (2h).

In a high-temperature discharge of normal-H₂ (ortho:para=3:1), one would expect an H₃⁺ ortho:para ratio of 1:1, as discussed by Cordonnier *et al.*⁹ These authors also

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TABLE I. Excitation and rotational temperatures measured using normal- and para-H₂. The “a” and “b” designations identify temperatures measured in close succession. The absorbance values are given in 10⁻⁶ cm⁻¹.

	Feed gas	Absorbance			Temperature (K)	
		$R(1,1)^u$	$R(1,0)$	$R(2,2)^\ell$	T_{ex}	T_{rot}
1	normal-H ₂	0.35	0.84	...	105	...
2	para-H ₂	0.41	...	0.07	...	62
3a	normal-H ₂	1.32	2.83	...	77	...
3b	normal-H ₂	1.32	...	0.43	...	85
4	normal-H ₂	0.25	0.56	...	86	...
5a	normal-H ₂	0.98	2.1	...	77	...
5b	normal-H ₂	0.98	...	0.28	...	79

calculated the expected ortho:para ratio of H₃⁺ for a para-enriched H₂ discharge and found an enhancement in para-H₃⁺, in agreement with their experiments. These calculations took a statistical approach, assuming that product states will be formed from combinations of reactant states according only to the constraints imposed by nuclear spin conservation. While this assumption is reasonable at high temperatures, it will break down at lower temperatures where (for example) there may be insufficient thermal energy to convert $J=0$ para-H₂ to $J=1$ ortho-H₂. New approaches to solving this problem have recently been proposed^{12,13} and will need to be taken into account in plasma modeling.

The present study was motivated by a dissociative recombination experiment requiring a cold, highly enriched para-H₃⁺ plasma.¹⁴ The work described in this Communication measured the para-H₃⁺ enrichment obtained when using an enriched para-H₂ feed gas along with dilutions intended to minimize the frequency of the hop (2h) and exchange (2e) reactions in the plasma. The experimental setup consisted of a closed-cycle helium cryostat capable of producing highly enriched para-H₂ (~99.99%) and a system for testing the level of enrichment.¹⁵ The plasma was generated by a pulsed solenoid source, and the para-H₃⁺ enrichment was measured using a continuous-wave cavity ringdown spectrometer built around a mid-IR difference frequency generation laser. Software was developed in order to synchronize the ringdown events with the pulsed source. The spectrometer was capable of probing transitions from the lowest H₃⁺ states: $R(1,1)^u$, $R(1,0)$, and $R(2,2)^\ell$ (see Ref. 16 for a description of the notation). A detailed discussion of the spectrometer, pulsed source hardware, and synchronization software can be found in an online supplement¹⁷ and in Ref. 18.

The experimental measurements had the following three objectives: (1) to determine the temperature of the expansion, (2) to measure the para-H₃⁺ enrichment that resulted from using highly enriched para-H₂, and (3) to observe the effect of dilution in an inert carrier gas on the fraction of para-H₃⁺ in the expansion.

The temperature of the expansion was measured by comparing the relative abundances of the para and ortho spin modifications of H₃⁺ formed from a normal-H₂ precursor gas (where ortho:para=3:1). This so-called excitation temperature (T_{ex}) has often been used as a proxy for the rotational

temperature (T_{rot}).¹⁹⁻²¹ The excitation temperature can be calculated using the equation

$$\frac{N_{(1,0)}}{N_{(1,1)}} = \frac{g_{(1,0)}}{g_{(1,1)}} e^{-\Delta E_{1,0-1,1}/k_B T_{\text{ex}}}, \quad (3)$$

where the ratio of nuclear spin degeneracy $g_{(1,0)}/g_{(1,1)}=4/2=2$ and $\Delta E_{1,0-1,1}=22.84$ cm⁻¹.¹⁶ In place of $N_{(1,0)}$ and $N_{(1,1)}$, we used the normalized peak absorbances of the rovibrational transitions $R(1,0)$ and $R(1,1)^u$ for ortho- and para-H₃⁺, respectively, divided by the squares of their transition dipole moments, $\mu_{R(1,0)}^2=0.0259$ D² and $\mu_{R(1,1)^u}^2=0.0158$ D². These transitions are separated by only 0.32 cm⁻¹, which made it easy to measure the peaks in quick succession. The results are presented in Table I.

In some instances, the rotational temperature itself was measured using transitions from the two lowest para-H₃⁺ rotational states: $R(1,1)^u$ and $R(2,2)^\ell$. T_{rot} was calculated using an equation similar to Eq. (3), with $\Delta E_{(2,2)-(1,1)}=105.2$ cm⁻¹ (Ref. 16) and applicable degeneracy terms, along with Einstein A coefficients.²² In all cases there was good agreement between T_{rot} and T_{ex} .

The temperature of the expansion was sensitive to the condition of the poppet as well as how tightly the poppet was seated in the source pinhole. The probe region was approximately 3.8 cm downstream of the electrode and about 4 mm in front of a skimmer. Measurements of the temperature were taken throughout the experiment. If the temperature was too hot (>100 K), the poppet would be “tuned” or replaced before proceeding. As can be seen from Table I, the typical temperature in the expansion was between 60 and 100 K, and the variations were likely due to the changing conditions of the poppet.

It is unclear why we did not observe temperatures colder than 60–100 K in our expansion. This same source produced ions at $T_{\text{ex}}=20$ –60 K a few years earlier.¹⁹ One possible cause was the gas-pulse/discharge-pulse sequencing. In the present experiment the gas pulse was embedded in a longer voltage pulse, which could have resulted in additional heating.

The intensities of the $R(1,0)$ ortho-H₃⁺ and the $R(1,1)^u$ para-H₃⁺ peaks were measured for normal and highly enriched (99.99%) para-H₂ precursor gases. The purpose of

TABLE II. The para- H_3^+ fraction observed with two different para- H_2 enrichments, including argon dilution results for the higher enrichment. A Boltzmann distribution for $T_{\text{rot}}=80$ K has been applied.

Starting para- H_2 (%)	Percent H_2^a	para- H_3^{+b} (%)
25	100	49.1 ± 2.4
99.99	100	78.5 ± 2.2
	15	78.0 ± 1.8
	5	70.9 ± 2.2
	0.8	83.3 ± 1.8

^aThe dilution was carried out using pressure ($P_{\text{H}_2}/(P_{\text{H}_2}+P_{\text{Ar}})$).

^bThe reported errors are calculated from the standard deviation (1σ) of multiple measurements at a particular point and a temperature uncertainty of ± 20 K.

these measurements was to quantitatively characterize the dependence of the para- H_3^+ fraction in the plasma on the para enrichment of the precursor gas. The simple equation,

$$\% \text{ para-}\text{H}_3^+ = \frac{\sum N_{\text{para}}}{\sum N_{\text{para}} + \sum N_{\text{ortho}}}, \quad (4)$$

was used to derive the para- H_3^+ percentage, where the $\sum N$ values were calculated using the measured intensities of the para- and ortho- H_3^+ ground state transitions. To go from the ground state intensities to the various $\sum N$, it was assumed that the rotational states within the para and ortho manifolds were thermally populated. Boltzmann distributions were applied assuming $T_{\text{rot}}=80 \pm 20$ K (based on the temperature measurements described above). At 80 K, almost 25% of para- H_3^+ ions are in rotationally excited states, whereas only 4% of ortho- H_3^+ are excited out of the ground state. The derived para- H_3^+ percentages are shown in Table II.

As expected, a discharge of normal- H_2 (25% para- H_2) gave results consistent with “normal- H_3^+ ” (50% para). However, using a highly enriched sample of para- H_2 in the discharge resulted in a plasma with $\sim 78.5 \pm 2.2\%$ para- H_3^+ . Figure 1 depicts the changes in peak heights of $R(1,0)$ and $R(1,1)^u$ as the enrichment of the para- H_2 precursor gas was increased from that of normal- H_2 to 99.99%.

Measurements were also taken using dilutions of para- H_2 in a nonhydrogenic gas to reduce the number of

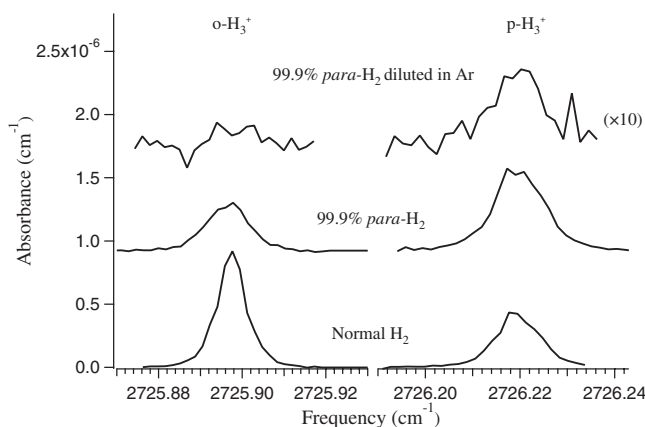


FIG. 1. Comparison of the spectra for H_3^+ for various precursor gases. Increasing the para- H_2 enrichment of the feed gas resulted in a higher enrichment of para- H_3^+ . The plots are shifted vertically for clarity.

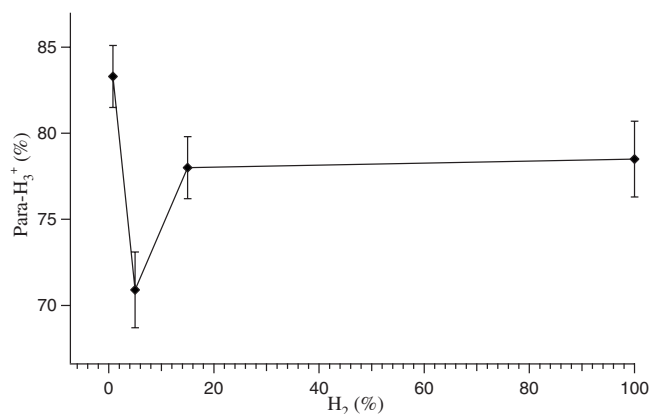


FIG. 2. The para- H_3^+ fraction vs argon dilution for 99.99% para- H_2 . Uncertainties are 1σ .

reactions between the para- H_3^+ ions and H_2 . The rate of reaction (2) for a given H_3^+ ion goes as $k[\text{H}_2]$, where k is the rate constant and $[\text{H}_2]$ is the number density of H_2 . If the overall number of molecules in the expansion remains the same, but $[\text{H}_2]$ is reduced by dilution in an inert gas, then the number of interactions between H_3^+ and H_2 will decrease. Thus, dilution will reduce the deleterious effect of the exchange reaction (2e) on the para- H_3^+ enrichment of the plasma. As discussed earlier, the exchange is the primary mechanism by which para- H_3^+ is converted to ortho- H_3^+ in para-enriched plasmas.

The dilutions were carried out by premixing the desired pressures of H_2 and argon or neon in order to provide 2 atm of backing pressure for the source. In all cases, the H_3^+ signal was substantially attenuated (by one or two orders of magnitude) by the dilution, as can be seen in Fig. 1. Not surprisingly, the results of the dilution experiments, graphically depicted in Fig. 2, show that the para- H_3^+ fraction has a dependence on the extent of the dilution. When the hydrogen was diluted between 5% and 15% in argon, an unexpected decrease in the fraction of $[\text{para-}\text{H}_3^+]/[\text{total } \text{H}_3^+]$ in the plasma was observed. The reason for this decrease is not understood at present but could have an impact on Ar- H_3^+ action spectroscopy schemes.^{23–25} Despite this, there was an increase in the para- H_3^+ fraction when H_2 was diluted to $\sim 1\%$ in argon.

The para- H_3^+ fraction was also measured in a neon carrier gas. The 10% dilutions in neon resulted in a signal similar to that of the 15% dilution in argon; however, when an $\sim 1\%$ dilution was analyzed, the H_3^+ signal was almost completely quenched.

In conclusion, we have observed for the first time the effects of the nuclear spin selection rules on the reaction between H_3^+ and H_2 at low temperature and exploited them to produce a source of rotationally cold and highly para-enriched H_3^+ . By diluting 99.99% para- H_2 in argon to $\sim 1\%$ by pressure, we have achieved a further enrichment to 83.3% para- H_3^+ . We have also observed unexpected behavior in the derived para- H_3^+ fraction at intermediate argon dilutions, which warrants further investigation, perhaps by simultaneous laser and mass spectroscopic measurements. Such a source can be used for reaction dynamics experiments be-

tween H_2 and H_3^+ , along with experiments that measure properties of para- H_3^+ enriched plasmas at astrophysically relevant temperatures.

We are presently in the process of extending these measurements to a wider range of both temperature and para- H_3^+ enrichment using a more reliable source based on a piezo valve²⁶ as well as a cryogenically cooled hollow cathode discharge. These measurements should provide more insight into the dynamics of reaction (2) and, in particular, into the branching ratio of reactions (2i), (2h), and (2e), and will be presented in a future publication.

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