Experimental study of para- and ortho-\(H_3^+\) recombination

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Abstract. Recombination of \(H_3^+\) with electrons is a key process for many plasmatic environments. Recent experiments on storage ring devices used ion sources producing \(H_3^+\) with enhanced populations of \(H_3^+\) ions in the para nuclear spin configuration to shed light on the theoretically predicted faster recombination of para states. Although increased recombination rates were observed, no \textit{in situ} characterization of recombining ions was performed. We present a state selective recombination study of para- and ortho-\(H_3^+\) ions with electrons at 77 K in afterglow plasma in a He/Ar/H\(_2\) gas-mixture. Both spin configurations of \(H_3^+\) have been observed \textit{in situ} with a near infrared cavity ring down spectrometer (NIR-CRDS) using the two lowest energy levels of \(H_3^+\). Using hydrogen with an enhanced population of \(H_2\) molecules in para states allowed us to influence the \([\text{para-}H_3^+]/[\text{ortho-}H_3^+]\) ratio in the discharge and in the afterglow. We observed an increase in the measured effective recombination rate coefficients with the increase of the fraction of para-\(H_3^+\). Measurements with different fractions of para-\(H_3^+\) at otherwise identical conditions allowed us to determine the binary recombination rate coefficients for pure para-\(H_3^+\) at 77 K:

\[
a_{\text{pa}}(77\text{ K}) = (2.0\pm0.4)\times10^{-7}\text{ cm}^3\text{s}^{-1}
\]

1. Introduction

The recombination of \(H_3^+\) with electron has been a long-standing issue in plasma physics for over 50 years, as both a theoretical and an experimental subject. Considering that this is one of the most important processes in the interstellar medium, planetary atmospheres [1,2] and in many technological types of plasma, it comes as no surprise that the enormous effort was put into its understanding. But despite best efforts the dissociative recombination of \(H_3^+\) has kept its secrets for a long time. Recently theoretical predictions made significant progress when the non-Born-Oppenheimer Jahn-Teller coupling was added to the calculations. Predictions for binary dissociative recombination rate coefficients of \(H_3^+\) ions with electrons at low energies (< 1 eV) [3,4,5,6] agree well with measurements from storage rings [7,8]. Large difference in the recombination rate for different nuclear spin (para and ortho) states of \(H_3^+\) at temperatures below 300 K was predicted too [6]. Although measurements on storage rings are showing an increase of the recombination rate coefficient when using \(H_3^+\) ions with enhanced population of para states [9,10,11], the beam experiments were made without \textit{in situ} determination of the spin state and rotational excitation of recombining ions and so the theoretical predictions could not have been fully tested [11,12]. The ratio of the thermal rate coefficients (para-\(H_3^+/\text{ortho-}H_3^+\)) observed in recent CRYRING experiment [9] is at 77 K equal \sim1.5 while theory [5] predicts ratio \sim3.

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In afterglow experiments, using a He/Ar/H₂ gas-mixture, H3⁺ ions can have several collisions with H₂ and thousands of collisions with He prior to recombination. Observed recombination rate coefficients are referred to as effective, because they are determined from plasma decay and several processes can influence the decaying plasma. By studying dependences of the effective recombination rate coefficient on experimental parameters it is possible to determine the rate coefficients for particular processes, the rate coefficient of binary recombination in particular.

Collision with H₂ can change the nuclear spin state of H₃⁺ via formation of the (H₂⁺)° complex [13,14,15,16]. Number density of H₂ and its spin state composition are therefore important parameters in H₃⁺ low temperature plasmatic experiments devoted to measurements of recombination rate coefficients. In such experiments the para-H₃⁺/ortho-H₃⁺ ratio has to be measured and considered in data evaluation and interpretation. For an extensive review of experiments and previous results see e.g. reviews [8,11,12,17] and book by Larsson and Orel [18].

We will use the following notation further: nuclear spin states with para and ortho symmetry of H₂ are designated as para-H₂ (or shortly ³H₂), ortho-H₂ (⁵H₂) and equivalently for H₃⁺. As normal hydrogen (⁴H₂) we will designate hydrogen with populations of ³H₂ and ⁵H₂ corresponding to thermal equilibrium at 300 K (25% of ³H₂). Para enriched hydrogen (⁴H₂) stands for hydrogen with populations of ³H₂ higher than 25%.

If the ortho- and para-H₃⁺ populations are not in thermodynamic equilibrium, then their actual densities in an experiment have to be measured. In H₃⁺ dominated low temperature plasma the sum of concentrations of both spin states of H₃⁺ corresponds to the electron density, [⁴H₃⁺] + [³H₃⁺] = nₑ. From the measured evolution of the electron density the effective recombination rate coefficient can be obtained (see [19] for the discussion). The balance equation for electrons is:

\[
\frac{dn_e}{dt} = -(\alpha_{eff} f + \alpha_{eff} f)n_e - \frac{n_e}{\tau_D} = -\alpha_{eff}n_e^2 - \frac{n_e}{\tau_D},
\]

where \(f\) and \(f\) denotes the fraction of H₃⁺ ions in para and ortho states respectively, \(\tau_D\) is the time constant of ambipolar diffusion, \(\alpha_{eff}\) and \(\alpha_{eff}\) are effective recombination rate coefficients for pure para-H₃⁺ and ortho-H₃⁺, respectively. \(\alpha_{eff} = \alpha_{eff} f + \alpha_{eff} f\) is the overall effective recombination rate coefficient which is determined from the electron density decay during the afterglow.

Measuring the effective recombination rate coefficient \(\alpha_{eff}\) at least at two different para-H₃⁺/ortho-H₃⁺ ratios, at otherwise identical conditions, one can simply derive the separate effective recombination rate coefficients for para- and ortho-H₃⁺. Thanks to spin selection rules at low temperatures < 300 K [15,16,20,21] one can change the para-H₃⁺/ortho-H₃⁺ ratio when using para enriched hydrogen as a reactant (see discussions and experiments in refs. [8,9,11,13,14,22]). Measurements at different helium concentrations offer the possibility to extract values of the binary and ternary recombination rate coefficients for the individual spin states (for a detailed discussion of the ternary process see previous papers of our group [23,24,25,26,27]).

Figure 1. Schematic drawing of the used optical cavity, discharge tube and microwave cavity. 10 mW DFB diode laser with \(\lambda \lambda \sim 2 \text{ MHz}\) was used in the experiment. With reflection of the mirrors \(R > 99.95\%\) we obtained typical baseline ring-down time ~30 µs.
2. Experimental apparatus

Pulsed microwave (µW) discharges were periodically ignited in a He/Ar/H₂ gas mixture. Temperatures of ~77 K were achieved by immersing the discharge tube into liquid nitrogen (see figure 1). Fast high voltage switch allowed us to turn off the incident µW power within 50 µs. Very low incident µW power (15 W) has been used to prevent heating of ions. Physical dimensions of the µW resonator limited the discharge column to ~5 cm of length.

To obtain decay curves of the two lowest rotational energy levels of H₃⁺ we used a near infrared cavity ring-down spectrometer (NIR-CRDS) with synchronous detection capabilities. For each ring-down event the time of data acquisition start was recorded, relative to the discharge cycle. More detailed description of the used apparatus can be found in [28,29] and in references therein. Pressures from 200 Pa to 1000 Pa were used to make the Doppler broadening the main broadening mechanism, in order to extract ion temperature information from absorption line profiles. Para enriched hydrogen was created in line during the experiments, by passing the hydrogen through an Fe₂O₃ catalyst cooled to temperatures below 20 K.

Figure 2. Panel (a) and (b): Observed absorption line profiles measured with para enriched H₂ used as precursor and 15 W of incident µW power. Other parameters are given in the legend. Panel (c): An example of evolution of ion temperature during the µW discharge.

Figure 3. Upper panel: An example of the measured concentration evolutions during the whole discharge cycle using para enriched H₂ as precursor. Lower panel: Corresponding ["H₃⁺"]/["H₃⁺"] ratio.

Figure 4. Upper panel: Example of ["H₃⁺"] and ["H₃⁺"] measured at the end of the discharge as a function of ℎ number density, with [He] ~ 2.7x10¹⁷ cm⁻³ and [Ar] ~ [H₃]. Lower panel: The corresponding dependence of the ["H₃⁺"]/["H₃⁺"] ratio on ["H₂"].
3. Results

As mentioned in the introduction, all measurements were done on transitions from the two lowest ro-vibrational levels of $\mathrm{H}_3^+$. That is for para-$\mathrm{H}_3^+$ the transition $3\nu_2(2,0)\rightarrow 0\nu_2(1,0)$ and $3\nu_2(2,1)\rightarrow 0\nu_2(1,1)$ for ortho-$\mathrm{H}_3^+$. Observed Doppler broadened absorption line profiles of $\mathrm{H}_3^+$ indicate the ions temperature of $(80\pm15)$ K during the discharge (see examples plotted in figures 2a and 2b). We have measured the line-widths for different time intervals during the discharge and the resulting ion temperature evolution (figure 2c) indicates that ions are not heated in the discharge. During the afterglow the concentration, and the corresponding absorption line intensity, falls down rapidly and obtaining a reliable temperature is difficult. Considering that already during the discharge the ion temperature is close to the buffer gas and wall temperature of 77 K, we can safely assume that it is not higher during the afterglow.

Since every ion undergoes several thousand collisions with He atoms prior to its recombination, we assumed that populations of higher rotational energy levels of both $\mathrm{H}_3^+$ spin configurations are in thermal equilibrium in their own respective spin symmetry manifold. From observed absorption evolutions at line center, together with the information about ion temperature, the evolutions of $[^3\mathrm{H}_3]^+\;\mathrm{and}\;[^1\mathrm{H}_3]^+$ were calculated (see examples in figures 3,5,6). The overall $[^3\mathrm{H}_3]^+/[^1\mathrm{H}_3]^+$ ratio is then calculated from the measured data for each set of experimental conditions.

![Figure 5. Examples of $[^3\mathrm{H}_3]^+$ decay curves measured at different $[^3\mathrm{He}]$ and at fixed $[^3\mathrm{He}]=2.7\times10^{17}$ cm$^{-3}$.](image1)

![Figure 6. An example of $[^1\mathrm{H}_3]^+$ decay curves measured at different $[^3\mathrm{He}]$, and very low hydrogen density $[^1\mathrm{H}_3]=7\times10^{12}$ cm$^{-3}$ and $[^3\mathrm{Ar}]=2\times10^{12}$ cm$^{-3}$.](image2)

Formation of $\mathrm{H}_3^+$ during a $\mu$W discharge in gas mixture is a very complex process. The presence of all reactant gases in the discharge and afterglow calls for a very cautious setting of all experimental parameters in order to obtain reliable measurements from which the effective recombination rate coefficient can be determined. For reliable measurements we need at the beginning of the afterglow high plasma density $n_e \sim 10^{13}$ cm$^{-3}$. This leads in early afterglow to a plasma decay with time constant in the order of 0.1 ms. To exclude overlapping of $\mathrm{H}_3^+$ formation with $\mathrm{H}_3^+$ recombination, $\mathrm{H}_3^+$ dominated afterglow has to be formed within 0.1 ms after discharge. To find the most suitable conditions for obtaining effective recombination rate coefficients, we have measured decay curves at a wide range of experimental conditions. The overall number density of $\mathrm{H}_3^+$ ions formed in the discharge increases with increasing number density of $\mathrm{H}_2$ ($^3\mathrm{H}_2$ or $^1\mathrm{H}_2$) (see figure 4). The kinetics of $\mathrm{H}_3^+$ formation was discussed in many publications (see e.g. [30] and references therein) so we will not go to any details here. In present study we have used calculations to obtain optimal conditions for the experiment. In addition we measured $[^1\mathrm{H}_3]^+$ decay at a broad range of conditions to obtain dependences of $[^1\mathrm{H}_3]^+$ on helium and hydrogen densities. In figure 5, decay curves measured with several $[^3\mathrm{He}]$ are
plotted. From the decay curves at $H_2$ concentrations lower than $5 \times 10^{13}$ cm$^{-3}$ (figure 5) one can clearly see that the $H_3^+$ formation process still continues in the afterglow and influences the shape of the decay curves thus making effective recombination rate coefficient extraction virtually impossible. Only at [H$_2$] $> 10^{14}$ cm$^{-3}$ is the decay dominated by recombination and can be described by constant $\alpha_{eff}$ during the afterglow. The kinetic model is supporting the finding that the para/ortho $H_3^+$ conversion by reaction with $H_2$ is fast enough to keep the para/ortho $H_3^+$ ratio constant, even at high electron densities.

![Figure 7. Dependence of the relative population of para-$H_3^+$ on the para enrichment of the precursor $H_2$. Measured at the end of the discharge where the ratio is constant (see figure 3). The arrow indicates data measured with normal hydrogen containing 25% of para-$H_2$ and 75% of ortho-$H_2$.](image)

We stress here that, because of high electron number density, the plasma decay in present experiments is many times faster than decays observed in AISA and FALP experiments, where typically the first 10 ms of decays are excluded from evaluation of recombination rate coefficients [30,31].

We also studied dependence of decay in early afterglow on [He]. An example of data obtained at low [H$_2$] and with several [He] are given in figure 6. Measurements at low [H$_2$] ($\sim 7 \times 10^{12}$ cm$^{-3}$), where the slow formation is most significant, show that formation of $H_3^+$ is faster at higher pressures. We stress again that these findings are not in contradiction with observations at the AISA apparatus where observation times were an order of magnitude longer.

Considering the observed influence of $H_2$ and He number densities on the formation of $H_3^+$, we adjusted both densities complementarily in order to obtained reliable decay curves for the determination of the effective recombination rate coefficients at various experimental conditions.

To change the ratio of [$^3H_3^+$]/[$^1H_3^+$] in the discharge and afterglow $^1H_2$ has been used. The fraction of $^3H_2$ molecules after conversion by Fe$_2$O$_3$ catalyst has been determined by nuclear magnetic resonance to be 87$\pm$5%. Dependence of the [$^3H_3^+$]/[$^1H_3^+$] ratio on the para enrichment of the precursor $H_2$ was measured at different conditions (see examples in figure 7). Final experiments with para enriched $H_2$ were performed with [$^3H_3^+$] fraction of (68$\pm$5)% in all measurements with $^1H_2$ the overall fraction was $\sim$ 50%, independent of $H_2$, Ar and He number density (see figures 7,8).

For each set of experimental conditions densities of [$^3H_3^+$] and [$^1H_3^+$] were measured. Decay curves measured with $^1H_2$ show that the [$^3H_3^+$]/[$^1H_3^+$] ratio is constant during the afterglow (see examples in figure 8). As was already mentioned, electron density decays were obtained by summing measured [$^3H_3^+$] and [$^1H_3^+$]. The electron density decay curves were fitted to obtain the values of effective recombination rate coefficients $\alpha_{eff}$. The $\alpha_{eff}$ obtained in experiments with $^1H_2$ and $^3H_2$ are plotted in figure 9. It is evident that the values of $\alpha_{eff}$ are higher for experiments with para enriched hydrogen. The measurements indicate very low values for the rate of the ternary helium assisted recombination of both para- and ortho-$H_3^+$ (figure 9). This is consistent with our previous experiments with normal $H_2$ [24]. Nevertheless, further measurements are needed to make quantitative conclusions about the
particular values of both ternary rate coefficients. Extrapolating effective recombination rate coefficients linearly to zero He density, for both \(^3\)H\(\text{_2}^+\) and \(^4\)H\(\text{_2}^+\) measurements, and using the average fraction \([^3\text{H}_2^+]\) of 68\% and 50\%, for \(^3\)H\(\text{_2}^+\) and \(^4\)H\(\text{_2}^+\), respectively, we obtained the following binary recombination rate coefficients: for para-H\(_3^+\), \(^p\alpha_{\text{bin}} = (2.0\pm0.4)\times10^{-7}\ \text{cm}^3\ \text{s}^{-1}\), and ortho-H\(_3^+\), \(^o\alpha_{\text{bin}} = (4\pm3)\times10^{-8}\ \text{cm}^3\ \text{s}^{-1}\).

4. Summary
Using NIR-CRDS we have measured the concentration evolution of para- and ortho-H\(_3^+\) during the microwave discharge and afterglow in He/Ar/H\(_2\) gas-mixture at various experimental conditions in order to determine optimal conditions for measurements of recombination rate coefficient of H\(_3^+\) ions. The measurements with normal hydrogen and hydrogen with higher relative population of para-H\(_2\) (\(^4\)H\(\text{_2}\) and \(^3\)H\(\text{_2}\)) showed that the \([^4\text{H}_2^+]\)/[^3\text{H}_2^+] ratio is higher when using para enriched hydrogen. By measuring \(\alpha_{\text{eff}}\) at two different relative populations of para- and ortho-H\(_3^+\) over a broad range of [He] we determined binary recombination rate coefficients for pure para-H\(_3^+\) and pure ortho-H\(_3^+\) at 77 K. The obtained values are in excellent agreement with theoretical predictions [6]. Our measurements show that at 77 K the binary recombination rate coefficient for para-H\(_3^+\) is approximately 5 times larger than for ortho-H\(_3^+\).

**Figure 8.** The measured decay curves of \(^4\)H\(_3^+\) and \(^3\)H\(_3^+\), using para enriched hydrogen (\(^3\)H\(\text{_2}\), top panel) and normal hydrogen (\(^4\)H\(\text{_2}\), middle panel). Obtained \(n_e\) in both experiments are also plotted. The variations of the ratio \([^4\text{H}_3^+]/[^3\text{H}_3^+]\) in experiments with \(^4\)H\(_2\) and \(^3\)H\(_2\) are plotted in lower panel.

**Figure 9.** The effective recombination rate coefficients measured with normal and para enriched \(^3\)H\(_2\) in He/Ar/H\(_2\) afterglow experiment at 77 K. NIR-CRDS was used for in-situ measurements of para-H\(_3^+\) and ortho-H\(_3^+\) number densities.
This is the first time that the recombination rate coefficients for para-H$_3^+$ and ortho-H$_3^+$ were determined in experiment with direct in situ determination of densities of para-H$_3^+$ and ortho-H$_3^+$ ions. Further studies are in progress.

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