Nuclear Spin Effect on Recombination of $H_3^+$ Ions with Electrons at 77 K

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Utilizing different ratios of para to ortho $H_2$ in normal and para enriched hydrogen, we varied the population of para-$H_3^+$ in an $H_3^+$ dominated plasma at 77 K. Absorption spectroscopy was used to measure the densities of the two lowest rotational states of $H_3^+$. Monitoring plasma decays at different populations of para-$H_3^+$ allowed us to determine the rate coefficients for binary recombination of para-$H_3^+$ and ortho-$H_3^+$ ions: $\alpha_{\text{eff}}(77 \text{ K}) = (1.9 \pm 0.4) \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$ and $\alpha_{\text{eff}}(77 \text{ K}) = (0.2 \pm 0.2) \times 10^{-7} \text{ cm}^3 \text{s}^{-1}$.

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Introduction.—$H_3^+$ is the dominant ion in many types of hydrogen-containing plasmas including astrophysically relevant plasmas [1,2]. It is the simplest polyatomic ion; its properties are well known [3,4]. The recombination of $H_3^+$ has been studied for over 50 years [5,6]. Only recently, the process of binary dissociative recombination (DR) of $H_3^+$ was described by going beyond the Born-Oppenheimer approximation and accounting for Jahn-Teller coupling [7]. The calculated cross sections [8,9] and the cross sections measured recently in storage ring experiments are approaching each other [10,11]. Presently, no reliable rate coefficient measured with storage rings below 300 K exists [12,13]. Only two years ago, it was demonstrated that the recombination rate coefficients (effective $\alpha_{\text{eff}}$) determined from plasma decay during an afterglow are composed of the binary and ternary process [14]. Taking this into the account, an agreement between experimental and calculated (DR) rate coefficients has been achieved for 77–300 K [15–19].

For temperatures below 300 K, the theory [9] of DR of $H_3^+$ predicts different values of recombination rate coefficients for different nuclear spin states of $H_3^+$ ($^p\alpha_{\text{DR}}$ and $^o\alpha_{\text{DR}}$ for para-$H_3^+$ with a total nuclear spin quantum number $I = 1/2$ and ortho-$H_3^+$ with $I = 3/2$, respectively). The qualitative reason is that at small collisional energies there are more Rydberg resonances of the neutral para-$H_3$ that can be populated during the electron-ion collisions. It is because there are more low energy rotational states of the ground vibrational state of para-$H_3^+$, for example, $(J, K) = (2, 2)$ and $(2, 1)$ (corresponding to energy of $\sim 151$ and 249 K). For ortho-$H_3^+$, the lowest rotational states of the ground vibrational state have relatively higher energies [for example, $(3, 0)$ corresponds to $\sim 650$ K]. More Rydberg resonances in para-$H_3^+$ enhances DR cross sections in para-$H_3^+$ more than in ortho-$H_3^+$ at low temperatures ($< 200$ K). The difference between $^p\alpha_{\text{DR}}$ and $^o\alpha_{\text{DR}}$ was partly confirmed by storage ring experiments [10].

The recent observations made towards several diffuse molecular clouds showed a large difference between excitation temperatures $T_{10}(H_2)$ and $T(H_3^+)$ derived from the relative intensities of lowest rotational levels of $H_2$ and $H_3^+$, respectively (for details, see Ref. [20]). These observations lead to the conclusion that in a reliable chemical model the nuclear spin dependences of the reactions, including recombination of para- and ortho-$H_3^+$, have to be considered. The dependences on spin, rotational excitation, and temperature have to be measured.

In this Letter, we report results of our pursuit of measuring the recombination rate coefficients $^p\alpha$ and $^o\alpha$ of pure para-$H_3^+$ and pure ortho-$H_3^+$. This is achieved by in situ determination of para-$H_3^+$ and ortho-$H_3^+$ densities in an $H_3^+$ dominated and recombination governed plasma in a He-Ar-$H_2$ mixture at 77 K. In the following, we will use upper left index $p$, $o$, $n$, and $e$ to indicate “para,” “ortho,” “normal,” and “para enriched,” respectively, e.g., $^pH_3$, $^oH_2$, $^nH_2$, and $^eH_2$. For para-$H_3^+$ and ortho-$H_3^+$ ions we use $^pH_3^+$ and $^oH_3^+$. Symbols $^p\gamma$ and $^o\gamma$ denote relative populations (fractions, $^p\gamma + ^o\gamma = 1$) of $H_3^+$ ions in the para and ortho state, respectively (i.e., $^p\gamma = [^pH_3^+]/[H_3^+]$ and $^o\gamma = [^oH_3^+]/[H_3^+]$). Normal ($^eH_2$) and para enriched ($^nH_2$) hydrogen were used in the experiments. In $^eH_2$, 1/4 of the H$_2$ molecules are in para and 3/4 in ortho states. In a low temperature hydrogen afterglow plasma, the main processes determining the density of $^pH_3^+$ and $^oH_3^+$ are diffusion and the following processes:

\[
^pH_3^+ + e \rightarrow ^p\alpha \text{ neutral products,}
\]

\[
^oH_3^+ + e \rightarrow ^o\alpha \text{ neutral products,}
\]

\[
^pH_3^+ \rightarrow ^p\gamma \rightarrow ^oH_3^+,
\]

where $^p\alpha_{\text{eff}}$ and $^o\alpha_{\text{eff}}$ are the effective rate coefficients of the overall recombination of $^pH_3^+$ and $^oH_3^+$, respectively. $\nu_{\text{po}}$ and $\nu_{\text{op}}$ are frequencies of $^pH_3^+$ to $^oH_3^+$ transitions and vice versa. If collisions with $^nH_2$ and $^eH_2$ dominate such processes, then $\nu_{\text{po}}$ and $\nu_{\text{op}}$ can be expressed as $\nu = k[^p\gamma H_2]$ where $k$ is a rate coefficient of the corresponding
nuclear spin changing reaction. The balance equations for \( ^7\text{H}_3^+ \) and \(^9\text{H}_3^+ \) are

\[
\frac{d[\ ^7\text{H}_3^+]}{dt} = -\rho \alpha_{\text{eff}}[^7\text{H}_3^+]n_e - \frac{[\ ^7\text{H}_3^+]}{\tau_D} - \nu_{\text{pol}}[^7\text{H}_3^+],
\]

\[
\frac{d[\ ^9\text{H}_3^+]}{dt} = -\rho \alpha_{\text{eff}}[^9\text{H}_3^+]n_e - \frac{[\ ^9\text{H}_3^+]}{\tau_D} - \nu_{\text{pol}}[^9\text{H}_3^+],
\]

where \( \tau_D \) is the time constant of ambipolar diffusion. If \([\ ^7\text{H}_3^+] + [\ ^9\text{H}_3^+] = n_e \), then we obtain by summing Eqs. (2) and (3)

\[
\frac{dn_e}{dt} = -(\rho \alpha_{\text{eff}} p f + \rho \alpha_{\text{eff}}^{\text{eff}}) n_e - \frac{n_e}{\tau_D} = -\rho \alpha_{\text{eff}} n^2 - \frac{n_e}{\tau_D}.
\]

We see that \( \alpha_{\text{eff}} \) determined from the decay of \( n_e \) \cite{21} depends on \( \rho f, \rho f^{\text{eff}}, \rho \alpha_{\text{eff}}, \) and \( \rho \alpha_{\text{eff}}^{\text{eff}} \). If \( \rho f \) and \( \rho f^{\text{eff}} \) are constant during the afterglow, the decay can be described by an effective recombination rate coefficient \( \alpha_{\text{eff}} = \rho \alpha_{\text{eff}} p f + \rho \alpha_{\text{eff}}^{\text{eff}} \). If \( \alpha_{\text{eff}} \) is measured at least for two different values of \( \rho f \), one can derive \( \rho \alpha_{\text{eff}} \) and \( \rho \alpha_{\text{eff}}^{\text{eff}} \). The overall recombination includes a binary and a ternary helium assisted recombination \cite{15–18}. In the first approximation we can write

\[
\alpha_{\text{eff}}(T, [\text{He}]) = \alpha_{\text{bin}}(T) + K_{\text{He}}(T)[\text{He}],
\]

where \( \alpha_{\text{bin}} \) and \( K_{\text{He}} \) are the corresponding rate coefficients; a similar relation can be written for \( \rho \alpha_{\text{eff}}^{\text{eff}} \) and \( \rho \alpha_{\text{eff}}^{\text{eff}} \).

Because of the weak coupling of the nuclear spin to the remaining degrees of freedom in \( \text{H}_3^+ \) and \( \text{H}_2 \), the probability of changing the nuclear spin by radiation is very low. In the present experiment, the main nuclear spin scrambling process is the reaction with \( \text{H}_2 \) via the formation of an \( (\text{H}_4^+)^+ \) reaction complex \cite{20,22–27}. This reaction allows efficient scrambling of the protons. Besides the dynamical details, rather stringent nuclear spin selection rules affect the ratio of \([\ ^7\text{H}_3^+]\) and \([\ ^9\text{H}_3^+]\) in the plasma \cite{20,22–28}. Therefore the change in \( \rho f \) can be achieved by using \( ^8\text{H}_2 \) instead of \( ^9\text{H}_2 \) \cite{20,23,29}. By performing the measurements with different \([\text{He}])\), the values \( \alpha_{\text{bin}} \) and \( K_{\text{He}} \) for the individual spin states have been obtained. For a detailed discussion of experiments with \( ^8\text{H}_2 \), see Refs. \cite{14,15,19}.

**Experiment.**—In the experiment, the plasma is formed in a pulsed microwave discharge in a fused silica tube cooled by liquid nitrogen to 77 K. The discharge was ignited in a mixture of \( \text{He}-\text{Ar}-\text{H}_2 \) (a typical composition 10\(^{18}\), 10\(^{14}\), 10\(^{13}\) cm\(^{-3}\) \cite{30}). Para enriched \( ^8\text{H}_2 \) was produced from \( ^9\text{H}_2 \) by using a \( \text{Fe}_2\text{O}_3 \) catalytic converter cooled below 20 K. Nuclear magnetic resonance spectroscopy was used to determine the fraction of \( ^8\text{H}_2 \) \( > (87 \pm 5)\% \).

The ion density was measured with a near infrared cavity ring down absorption spectrometer \cite{31,32}. The densities of the two lowest rotational states of the ground vibrational state of \( \text{H}_3^+ \) were measured by using the transition \( 3\nu_1^0(2,0) \leftrightarrow 0^2\nu_0^0(1,0) \) for \( ^7\text{H}_3^+ \) and \( 3\nu_1^0(2,1) \leftrightarrow 0^2\nu_0^0(1,1) \) for \( ^9\text{H}_3^+ \); for notation and details, see Refs. [31,32]. In a thermodynamic equilibrium at 77 K, these two lowest rotational states contain \( \approx 86\% \) of the population of \( \text{H}_3^+ \). The Doppler broadening of the absorption lines was measured to obtain the kinetic temperature of \( \text{H}_3^+ \). The measured kinetic temperature of ions in the active discharge was \( (80 \pm 15) \text{ K} \). Because of the high helium density \([\text{He}] = (2–18) \times 10^{17} \text{ cm}^{-3} \), the relaxation time for the electron temperature is below 1 \( \mu \text{s} \). In the early afterglow, the electron and ion temperatures relax, and in the later afterglow \( (\approx 50 \mu \text{s}) \), we can expect that the temperature of electrons and ions is 77 K.

Because of high \([\text{He}] \), \([\text{H}_2] \), and \( n_e \), any ion has on average \( 10^5 \) collisions with \( \text{He} \), 10 collisions with electrons \cite{33}, and more than 10 collisions with \( \text{H}_2 \) prior to its recombination. This is why it is safe to assume that during the afterglow the population of states within the \( ^7\text{H}_3^+ \) and

![Graph](https://example.com/graph.png)

FIG. 1 (color online). The decay curves measured for \( ^7\text{H}_3^+ \) and \( ^9\text{H}_3^+ \) using para enriched \( \text{H}_2 \) (\( ^9\text{H}_2 \), top panel) and normal \( \text{H}_2 \) (\( ^8\text{H}_2 \), middle panel). Obtained \( n_e \) are also plotted. The line indicated as (3, 3) in the middle panel is a decay curve for \( \text{H}_3^+ \) in the eponymous state. The fractions \( \rho f \) of \( ^7\text{H}_3^+ \) measured in experiments with \( ^8\text{H}_2 \) and \( ^9\text{H}_2 \) are plotted in the lower panel.
$^{3}\text{H}_3^+$ manifold is thermalized to 77 K and it is sufficient to measure densities of $^{3}\text{H}_3^+$ in the lowest rotational states, i.e., (1, 1) of $^{3}\text{H}_3^+$ and (1, 0) of $^{3}\text{H}_3^+$. This assumption was confirmed also by the measurement of a population distribution among (3, 3) metastable ortho state [24] and two aforementioned states in the $^{3}\text{H}_2$ discharge for temperatures in the 77–200 K range.

Results and discussion.—When using $^{3}\text{H}_2$ as precursor, we observed $^{p}f = \alpha_f = 0.5$; see Figs. 1 and 2. That holds for the whole $^{3}\text{H}_2$ density range used in the present experiments [(0.5–5) × 10^{14} cm$^{-3}$].

For each set of experimental conditions, the evolutions of $^{p}$[$^{3}\text{H}_3^+$] and $^{p}$[$^{3}\text{H}_3^+$] were measured and $n_v$ were calculated (Fig. 1). From these evolutions, we extracted $\alpha_{\text{eff}}$ and $^{p}f$. The first 50–100 μs of the decay are excepted from the analysis to exclude the formation-relaxation region. In Fig. 2 (upper panel), rate coefficients measured with $^{3}\text{H}_2$ at 77 K are plotted as a function of [He]. The data were fitted by using Eq. (5), and the recombination rate coefficients of $^{3}\text{H}_3^+$ with $^{p}f = \alpha_f = 0.5$ were obtained: $^{n}\alpha_{\bin}(77 K) = (1.0 \pm 0.2) \times 10^{-7}$ cm$^3$ s$^{-1}$ for the binary and $^{n}K_{\text{He}}(77 K) = (1.5 \pm 0.2) \times 10^{-25}$ cm$^6$ s$^{-1}$ for the ternary process. Earlier data obtained with a Langmuir probe in the flowing afterglow experiment (FALP) at (82 ± 5) K are also plotted for comparison [15].

Using $^{3}\text{H}_2$ as a precursor, we increased the fraction of $^{3}\text{H}_3^+$. The obtained $^{n}\alpha_{\text{eff}}$ and $^{p}f$ are plotted in Fig. 2. It is evident already from these plots that the recombination of $^{3}\text{H}_3^+$ is faster. From $^{n}\alpha_{\text{eff}}$ and $^{p}f$, measured with $^{3}\text{H}_2$, the values $^{p}\alpha_{\text{eff}}$ and $^{n}\alpha_{\text{eff}}$ for $^{3}\text{H}_3^+$ and $^{3}\text{H}_3^+$ were calculated. In these calculations, the dependence fitted through data measured with $^{3}\text{H}_2$ was used as a reference (full lines in Fig. 2 indicated as $^{n}\alpha_{\text{eff}}$). By fitting the data $^{p}\alpha_{\text{eff}}$ and $^{n}\alpha_{\text{eff}}$ with a linear dependence [Eq. (5)], we obtained corresponding binary and ternary recombination rate coefficients.

For $^{3}\text{H}_3^+$, $^{p}\alpha_{\bin} = (1.9 \pm 0.4) \times 10^{-7}$ cm$^3$ s$^{-1}$ and $^{p}K_{\text{He}} = (1.9 \pm 0.4) \times 10^{-25}$ cm$^6$ s$^{-1}$. For $^{3}\text{H}_3^+$, $^{n}\alpha_{\bin} = (0.2 \pm 0.2) \times 10^{-7}$ cm$^3$ s$^{-1}$ and $^{n}K_{\text{He}} < (1.1 \pm 0.4) \times 10^{-25}$ cm$^6$ s$^{-1}$. The results are summarized in Fig. 3—the agreement with FALP experiments [15,19] and with the theory [9] is excellent.

Summary.—By using a cavity ring down absorption spectrometer, the evolution of ortho-$^{3}\text{H}_3^+$ and para-$^{3}\text{H}_3^+$ densities has been monitored in situ during the afterglow. From such measurements, effective rate coefficients of recombination of $^{3}\text{H}_3^+$, for a particular para-$^{3}\text{H}_3^+$/ortho-$^{3}\text{H}_3^+$ ratio at 77 K, have been determined and the effective recombination rate coefficients of both spin modifications ($^{p}\alpha_{\text{eff}}$ and $^{n}\alpha_{\text{eff}}$) were obtained. The rate coefficients of the binary recombination of para-$^{3}\text{H}_3^+$ and ortho-$^{3}\text{H}_3^+$ ($^{p}\alpha_{\bin}$ and $^{n}\alpha_{\bin}$) were determined by measuring at different [He]. To our knowledge, this is the first study of $^{3}\text{H}_3^+$ recombination with in situ determination of the composition of the decaying plasma with respect to para and ortho states of $^{3}\text{H}_3^+$. 

FIG. 2 (color online). Dependencies of effective recombination rate coefficients on He density. Upper panel: Data from experiments with $^{3}\text{H}_2$ and ‘$^{3}\text{H}_2$’ ($^{p}\alpha_{\text{eff}}$ and $^{n}\alpha_{\text{eff}}$). Included are data obtained in the FALP experiment using $^{3}\text{H}_2$ (at 82 ± 5 K, open squares). Lower panel: Relative populations of $^{3}\text{H}_3^+$ (fraction $^{p}f$) measured in experiments using $^{3}\text{H}_2$ and ‘$^{3}\text{H}_2$.

FIG. 3 (color online). Measured binary recombination rate coefficients for normal $^{3}\text{H}_3^+$, ortho-$^{3}\text{H}_3^+$, and para-$^{3}\text{H}_3^+$ in comparison with FALP data for normal $^{3}\text{H}_3^+$ [14,15,19] and theoretical predictions [9]. Normal $^{3}\text{H}_3^+$ indicates data measured with normal $^{3}\text{H}_2$. TDE stands for thermodynamic equilibrium.
\( \text{H}_3^+ \). Since the majority of the ions is in the lowest rotational states of para and ortho modifications [(1, 1) and (1, 0)] at 77 K, it is the first time that binary recombination rate coefficients were obtained for ions in the ground vibrational, specific nuclear, and rotational states. The theoretical prediction made for binary DR [9] is in excellent agreement with our data. No reliable storage ring data below 300 K exists [13].

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