Binary recombination of para- and ortho-H$_3^+$ with electrons at low temperatures

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Results of an experimental study of binary recombination of para- and ortho-H$_3^+$ ions with electrons are presented. Near-infrared cavity-ring-down absorption spectroscopy was used to probe the lowest rotational states of H$_3^+$ ions in the temperature range of 77–200 K in an H$_3^+$-dominated afterglow plasma. By changing the para/ortho abundance ratio, we were able to obtain the binary recombination rate coefficients for pure para-H$_3^+$ and ortho-H$_3^+$. The results are in good agreement with previous theoretical predictions.

Keywords: H$_3^+$; dissociative recombination; cavity ring down spectroscopy; afterglow plasma

1. Introduction

The fundamental characteristics of the H$_3^+$ dissociative recombination (DR) [1] have been the subject of much interest for both theoretical and experimental physicists [2]. The discrepancies between measurements of the binary dissociative reaction rate and the theoretical complexity of this seemingly simple reaction led to a great deal of fruitful research on this process. The history of H$_3^+$ recombination studies has been adequately covered in several review articles [3–9]. Recently, both theory and experiment have converged to a value for the rate of this particular reaction. The theoretical treatment took a crucial leap forward in the understanding of the DR process after including the Jahn–Teller mechanism as the critical step in the initial electron-capture step of the DR reaction [10]. This resulted in a convergence with experimental DR data reported from ion storage rings where experimentalists had realized the impact of rotational excitation of the H$_3^+$ ions on the DR reaction rate, especially with respect to the importance of the DR process in interstellar molecular clouds [11–13]. Final convergence between theory and the remaining important experimental techniques, stationary and flowing afterglow, was reached after recognizing that a

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fast third-body reaction, not previously considered, stabilizes the recombination process in such plasmas \[4,14,15\]. However, recently it has been shown \[16,17\] that the assumption of rotationally cold H$_3^+$ ions in storage rings was not entirely correct \[17\]. This is important if we realize that the quantum mechanical calculations \[18\] predict a large difference in the low-temperature recombination of ions in para-H$_3^+$ and ortho-H$_3^+$ states. This has been qualitatively confirmed in storage-ring experiments using hydrogen with an enriched para fraction \[12,13,19\]. However, as has just been stated, the actual rotational population of the recombing ions has not been proved experimentally. In the present experiments, the stationary afterglow (SA) technique with spectroscopic in situ determination of the abundances of the recombing ions was used. Near-infrared cavity-ring-down absorption spectroscopy (NIR-CRDS) enabled in situ determination of the spin states, together with the kinetic and the rotational temperatures of the recombing ions. A similar approach was used in our recent study of binary recombination of para-H$_3^+$ and ortho-H$_3^+$ ions at temperatures close to 77 K \[20\]. In the present studies, we have extended the range of temperatures up to 200 K. Our previous measurements in H$_3^+$- and D$_3^+$-dominated plasmas at conditions similar to those in the present experiment \[4,14,15,21,22\] have shown that the H$_3^+$ ions recombine by both a binary process with a rate coefficient $\alpha_{\text{bin}}$, and a ternary helium-assisted recombination mechanism, with a rate coefficient $K_{\text{He}}$.

The plasma decay can then be described by an overall effective recombination rate coefficient:

$$\alpha_{\text{eff}} = \alpha_{\text{bin}} + K_{\text{He}}[\text{He}]. \tag{1.1}$$

Both rate coefficients can be obtained by measuring the dependence of $\alpha_{\text{eff}}$ on the helium density [He]. The possible effects of another ternary process—collisional radiative recombination (CRR) \[23,24\]—are discussed in detail elsewhere \[25\].

In the following, we will use left indices p, o, n and e to denote ‘para’, ‘ortho’, ‘normal’ and ‘para-enriched’ hydrogen (i.e. $^p$H$_2$, $^o$H$_2$, $^n$H$_2$ and $^e$H$_2$) and $^p$f$_3$ and $^o$f$_3$ to denote para and ortho fractions. $^p$H$_3^+$ and $^o$H$_3^+$ stand for para-H$_3^+$ and ortho-H$_3^+$, while $^p$f$_3$ and $^o$f$_3$ denote their fractions (i.e. $^p$f$_3 = [^p$H$_3^+]/[H$_3^+$] and $^o$f$_3 = [^o$H$_3^+]/[H$_3^+$]). If an index is missing, then the spin modification is not specified. Assuming that the plasma is quasi-neutral and that it contains no ions other than H$_3^+$ (i.e. $n_e = [^p$H$_3^+] + [^o$H$_3^+]$), then following the derivation in the study of Varju et al. \[20\], we can write the continuity equation for the electron number density $n_e$:

$$\frac{dn_e}{dt} = - (p\alpha_{\text{eff}}^p f_3 + o\alpha_{\text{eff}}^o f_3) n_e^2 - \frac{n_e}{\tau_D} = - \alpha_{\text{eff}}^e n_e^2 - \frac{n_e}{\tau_D}, \tag{1.2}$$

where $^o\alpha_{\text{eff}}$ and $^p\alpha_{\text{eff}}$ are the state-selected effective recombination rate coefficients for $^o$H$_3^+$ and $^p$H$_3^+$, respectively, $\alpha_{\text{eff}} = p f_3^p \alpha_{\text{eff}}^p + o f_3^o \alpha_{\text{eff}}^o$ is the overall (apparent binary) recombination rate coefficient for a given mixture of ortho and para ions, and $\tau_D$ is the characteristic time constant of the ambipolar diffusion. A linear relation similar to equation (1.2) holds also for $^p\alpha_{\text{eff}}$ and $^o\alpha_{\text{eff}}$ \[20\].

The data (see §3) show that at the H$_2$ and He densities used in the experiment, the fractions $^p$f$_3$ and $^o$f$_3$ are nearly constant during the afterglow. A measurement of $\alpha_{\text{eff}}$ for two or more different values of $^p$f$_3$, but under otherwise identical conditions (temperature, and density of He and H$_2$), then permits a determination.
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of the individual recombination rate coefficients \(p\alpha_{\text{eff}}\) and \(o\alpha_{\text{eff}}\). The fraction \(p_{f_3}\) can be enhanced from about 0.5 to 0.8 by using para-enriched hydrogen instead of normal hydrogen (for details, see [20,26]).

2. Experimental apparatus

The experimental apparatus is the same as that in our previous studies [20,26]. A pulsed microwave discharge generates a plasma in a tube (inner diameter of approx. 1.5 cm) cooled by liquid nitrogen. A mixture of He/Ar/H\(_2\) with a typical composition \(10^{17}/10^{14}/10^{14}\) cm\(^{-3}\) flows continuously along the discharge tube. Details of the ion formation reactions are given elsewhere [4,5,27]. ‘A para-hydrogen generator’ prepares samples of para-enriched H\(_2\) (\(^p\)H\(_2\)) [26]. The enrichment was measured by nuclear magnetic resonance spectroscopy (RNDr Jan Lang PhD 2010, personal communication). NIR-CRDS in the continuous wave modification (based on the configuration described by Romanini \textit{et al.} [28]) was developed in our laboratory for time-resolved studies [26,29,30]. The light source is a fibre-coupled distributed feedback laser diode with a central wavelength of 1381.55 nm, line-width less than 2 MHz, and maximum output optical power of 20 mW. During the experiment, the time-dependent optical absorption signals from the discharge and the afterglow are recorded. The measured absorption is then converted to ion concentrations. The kinetic temperature of the H\(_3^+\) ions and its evolution during the discharge and in the early afterglow were determined from the Doppler-broadened absorption line profiles by tuning the wavelength of the laser diode. All spectroscopic absorption measurements were performed on the second overtone transitions originating from the ground vibrational level of H\(_3^+\). The lowest rotational levels (1,0) (ortho, transition 3\(v_2^1(2,0) \leftarrow 0v_2^0(1,1)\)) and (1,1) (para, transition 3\(v_2^1(2,1) \leftarrow 0v_2^0(1,1)\)) of the vibrational ground state were monitored routinely. In some experiments, we also probed the higher-lying level (3,3) (ortho, transition 3\(v_2^1(4,3) \leftarrow 0v_2^0(3,3)\)). Here, and in the following discussion, the energy levels are labelled \((J, G)\) by their quantum numbers \(J\) and \(G\).

3. Experimental results: binary recombination of para-H\(^+_3\) and ortho-H\(^+_3\)

The measured electron density decay curves were analysed to obtain \(\alpha_{\text{eff}}\) for two particular values of \(p_{f_3}\) (further details can also be found in the study of Varju \textit{et al.} [20]). We carried out a systematic set of measurements that differed only in the value of \(p_{f_2}\) (\(p_{f_2} = 0.25\) when using \(^p\)H\(_2\) and \(p_{f_2} = 0.87\) using \(^o\)H\(_2\)), but under otherwise very similar conditions. The densities of the para (1,1), ortho (1,0) and ortho (3,3) states of H\(_3^+\) were monitored. Examples of data measured at 140 K with \(^p\)H\(_2\) and with \(^o\)H\(_2\) are plotted in figure 1\(a,b\), respectively. The middle panels of figure 1\(a,b\) show a large difference in the measured populations of the particular rotational states of H\(_3^+\) in both experiments. In this set of experiments, we obtained \(p_{f_3} \sim 0.5\) for \(^p\)H\(_2\), and \(p_{f_3} \sim 0.7\) for \(^o\)H\(_2\) (see the lower panels). Note that in both experiments, the values of \(p_{f_3}\) are nearly constant during the afterglow.

Assuming thermal equilibrium (TDE) within the para and ortho manifolds, we calculated from the densities of the ions in the (1,1) and (1,0) states the
Figure 1. (a) Upper panel: a typical example of the ion and electron decay curves measured during the afterglow in a He/Ar/\( {\text{H}}_2 \) gas mixture. The time \( t = 0 \) is taken to be at the beginning of the afterglow when the discharge is switched off. The measurements were made at 140 K and 1000 Pa of He and at the indicated densities of \( {\text{H}}_2 \) and Ar. Middle panel: the measured relative populations of the para (1,1), ortho (1,0) and ortho (3,3) states of \( {\text{H}}_3^+ \). Lower panel: the measured fraction of \( p_f \) of \( {\text{H}}_3^+ \). Note the constant value of \( p_f \) during the afterglow. (b) Similar to (a), but for data measured in a He/Ar/\( {\text{H}}_2 \) gas mixture. (Online version in colour.)

We have proved experimentally [25,26] that the assumption of TDE under our experimental conditions is correct. To obtain \( \alpha_{\text{eff}} \) from the measured electron density decay curves, we used direct fits to the data and, in addition, the more advanced ‘integral analysis’ technique [31]. We deliberately excluded the first 50–150\( \mu \)s of the afterglow decay from the data analysis because some new ions were probably still being formed (for details see [4,20,26,31]). The observed dependences of \( ^n\alpha_{\text{eff}} \) and \( ^e\alpha_{\text{eff}} \) on [He] at 140 K are shown in figure 2a. The corresponding fractions \( p_f \) are shown in figure 2c. Because \( ^n\alpha_{\text{eff}} \) and \( ^e\alpha_{\text{eff}} \) increase linearly with increasing [He], we can use equation (1.1) to obtain binary and ternary recombination rate coefficients for known para/ortho ratios. The values obtained with normal hydrogen (\( p_f = 0.5 \)) correspond to those expected under TDE. The present experiments with \( ^n\text{H}_2 \) also confirmed that \( p_f = 0.5 \) in our previous flowing afterglow with Langmuir probe (FALP) experiments [4,14,15,32]. Hence, the values of \( \alpha_{\text{bin}} \) and \( K_{\text{He}} \) from these experiments correspond to TDE.

The dependences of \( ^n\alpha_{\text{eff}} \) and \( ^e\alpha_{\text{eff}} \) on [He] were measured for four temperatures in the 77–200 K range. From those dependences and from the corresponding \( p_f \), we calculated the values of \( ^p\alpha_{\text{eff}} \) and \( ^o\alpha_{\text{eff}} \) for pure \( ^p\text{H}_3^+ \) and for pure \( ^o\text{H}_3^+ \), respectively. The binary recombination rate coefficients for pure \( ^p\text{H}_3^+ \) and for pure \( ^o\text{H}_3^+ \) were obtained by fitting the values of \( ^p\alpha_{\text{eff}} \) and \( ^o\alpha_{\text{eff}} \) (figure 2b) using equation (1.1). For further details on the data analysis, see Varju et al. [20]. The measured values of \( ^p\alpha_{\text{bin}} \), \( ^o\alpha_{\text{bin}} \), \( ^n\alpha_{\text{bin}} \) and values of \( ^n\alpha_{\text{bin}} \) from previous FALP experiments [4,14,15] are plotted in figure 3. The displayed errors of rate coefficients are 1\( \sigma \) errors, and systematic errors (mainly from determination of ion number densities) were estimated to be less than 10 per cent.
Figure 2. The measured dependences of the effective recombination rate coefficients on the He density at 140 K. (a) $\alpha_{\text{eff}}$ measured using $^n\text{H}_2$ (open circles) and $\alpha_{\text{eff}}$ measured using $^4\text{H}_2$ (filled circles). (b) The measured values $^p\alpha_{\text{eff}}$ and $^o\alpha_{\text{eff}}$ for pure $^p\text{H}_3^+$ (filled triangles) and pure $^o\text{H}_3^+$ (open triangles), respectively. (c) The fractions $p_{f_3}$ of $^p\text{H}_3^+$ measured in the experiments with $^n\text{H}_2$ and $^4\text{H}_2$. (Online version in colour.)

4. Discussion and conclusion

By using either normal or para-enriched hydrogen gas, we were able to form plasmas with different partial populations of $^p\text{H}_3^+$ (fractions, $p_{f_3}$) and $^o\text{H}_3^+$, and from the measured decay of the ion density, we evaluated the binary recombination rate coefficients for pure $^p\text{H}_3^+$ and $^o\text{H}_3^+$ ions. The temperature range covered in this study was 77–200 K. The results of this study show a strong dependence of the low-temperature binary recombination of $\text{H}_3^+$ ions on the nuclear spin states of the ions. The agreement between the experimental values ($^n\alpha_{\text{bin}}$, $^p\alpha_{\text{bin}}$ and $^o\alpha_{\text{bin}}$) and the theoretical values ($^n\alpha_{\text{DR}}$, $^p\alpha_{\text{DR}}$ and $^o\alpha_{\text{DR}}$) [18] is very good. Moreover, though the electron number density used in the present experiment was by an order of magnitude higher than in our previous FALP experiments using Langmuir probes [14], the agreement between the present $^n\alpha_{\text{bin}}$ values and those from the FALP experiments is very good over the whole temperature range. Because of this agreement at higher temperatures, where CRR is negligible, we conclude that the measured rate coefficients at 77 K do not depend on the electron density. From this, it follows that CRR has little to no effect on the plasma decay and that the obtained recombination rate coefficients

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Figure 3. The measured temperature dependences of the binary recombination rate coefficients $\alpha_{\text{bin}}^{n}$, $\alpha_{\text{bin}}^{p}$ and $\alpha_{\text{bin}}^{o}$. ‘Normal-$H_3^+$’ refers to data measured in the present experiments with $^9\text{H}_2$. Previous FALP data [4,14,15] measured with $^9\text{H}_2$ are indicated by filled circles. Combined SA-CRDS/FALP data at 100 K and 305 K [4,14] are indicated by a filled circle in a square. The lines indicate the theoretical rate coefficients for $^9\text{H}_3^+$, $^{10}\text{H}_3^+$ and for $^{13}\text{H}_3^+$ ions in TDE [18]. (Online version in colour.)

$p\alpha_{\text{bin}}$ and $o\alpha_{\text{bin}}$ correspond to the binary DR (for details see discussion in the study of Dohnal et al. [25]). Further results concerning ternary recombination have been published elsewhere [25], together with a detailed discussion of the equilibrium conditions in the recombining afterglow plasma and with an estimation of the effect of the CRR process.

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