Multicollision character of recombination of H$_3^+$ ions in afterglow plasma

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Abstract. Reported are studies of recombination of H$_3^+$ ions with electrons in flowing afterglow (FALP) experiment. Reported is observation of dependence of overall recombination process on He pressure and hydrogen partial pressure. The obtained data are in good agreement with previous stationary afterglow (AISA) results and clearly indicate the multicollision and multistep character of the recombination process. Proposed is scheme of overall recombination process.

1. Introduction
Recombination of H$_3^+$ ions with electrons is key process playing role in evolution of hydrogen containing laboratory and natural plasmas. Because of its importance in plasma physics, technology, astrophysics and theory, it is attracting broad attention for nearly 50 years. Over these years recombination of H$_3^+$ has become the “fundamental problem”. The results of H$_3^+$ recombination studies were for a long time very controversial [1,2,3]. The problems were also with interpretation of astronomical observations of H$_3^+$ [4,5]. The “enigma” of H$_3^+$ has been solved only very recently, with the inclusion of the non-Born-Oppenheimer Jahn-Teller coupling, which gave high rate of dissociative recombination of this ion [6,7]. The theoretical predictions were confirmed by very recent storage ring experiments. These experiments have used new type of ion sources, where ions prior to injection into the ring were rotationally and vibrationally cooled [8,9]. In contradiction with mentioned theory was just the measured increase [9,10] of the low energy recombination rate coefficient when the ion beam was enriched by para H$_3^+$ (the component with total nuclear spin ½). This was solved in the recently published theoretical work with higher accuracy of calculations [11]. Now the qualitative agreement of theory and storage ring experiments has been achieved. The theory now predicts that at temperatures below 100 K the recombination of para H$_3^+$ will be at low energies substantially faster than the recombination of ortho H$_3^+$.

The theory is in agreement with the storage ring experiments, but there are still some unsolved problems with recombination of H$_3^+$ ions. The main problem is that up to now there is no reliable interpretation of many plasmatic experiments which give very different values of recombination rate coefficient (see compilation in refs. [1,2,12]). In recent years we have studied in our laboratory the recombination of H$_3^+$ ions using stationary afterglow experiment AISA and we have observed the dependence of the recombination rate coefficients on partial pressure of hydrogen [12,13,14,15,16,17]. AISA was build to study slow recombination processes, nevertheless it has the main disadvantage of stationary afterglow experiments: the mixture of gases, here He, Ar and H$_2$, are exposed to discharge...
and long-lived excited species and radicals can be produced. These particles can influence the decay of the plasma and the apparent recombination rate coefficient determined from the decay of electron number density. We were trying to eliminate such uncertainties in our experiments. To identify recombining ions we build second stationary afterglow experiment, Test Discharge Tube (TDT). In TDT the density of recombining ions (H$_3^+$ (v=0)) was measured by NIR cavity ring-down absorption spectroscopy (CRDS) [18,19]. The TDT-CRDS studies were carried out only at relatively high hydrogen densities. The dependence on partial pressure of hydrogen was not measured. In the covered range of hydrogen partial pressures there is good agreement between TDT-CRDS and AISA results.

The dependence of recombination rate coefficient on partial pressure of H$_2$ observed in the AISA is clear proof that the recombination process is not pure binary dissociative recombination but it is a multi-collision process. Nevertheless the data from AISA and TDT-CRDS did not give enough information for the characterisation of this multicollisional process; the results were left without interpretation. We also didn’t any have theoretical prediction of a lifetime of a neutral H$_3^*$ formed in collision of H$_2^+ with electron. Nevertheless it was obvious that the recombination rate coefficient measured in AISA is an effective recombination rate coefficient and not the rate coefficient corresponding to the binary dissociative recombination (DR), which is measured in colliding beams experiments and which is calculated by theory of DR. In another words the recombination of H$_3^+$ in plasma differs from DR. Here we have in mind afterglow plasma in He buffer used in recombination studies.

The common feature of many experiments with H$_3^+$ dominated plasma was, that the plot of the reciprocal electron density (1/n_e) did not show linear dependence on decay time as it follows from the solution of the balance equation with the assumption of binary recombination process, typical e.g. for decay of O$_2^+$ dominated plasma [12]. In several experiments “evolution” of the recombination rate coefficient during an afterglow was observed [2,20]. First obvious explanation is vibrational excitation of recombining ions and relaxation during the afterglow [2]. On many occasions three-body character of the recombination process was discussed, but there was lack of clear experimental evidences. The problem of complex formation in electron-ion recombination of molecular ions including H$_3^+$ was discussed in paper of R. Johnsen and J.B.A. Mitchell [21]. In their paper many experimental evidences for formation of long-lived H$_3^*$ were discussed, nevertheless no quantitative results were given.

As was already mentioned the problem of stationary afterglow technique is, that in the process of plasma formation H atoms and some excited particles can be formed and they can later influence the process of plasma decay and hence the determination of apparent recombination rate coefficients. Even spectroscopic identification of recombining ions cannot exclude this “fingerprints of formation”. The flowing afterglow technique (Flowing Afterglow with Langmuir Probe - FALP) can solve the problem of formation by ignition of discharge in pure helium and formation of H$_3^+$ ions by sequential introduction of gases to already cold afterglow plasma.

2. Experiments
To create in the FALP experiment conditions at which the dependence on [H$_2$] was observed in AISA we have changed construction of flow tube, see Fig. 1. In FALP fast flow of He buffer gas is carrying decaying plasma along the flow tube. To obtain a long decay time of the afterglow plasma the used pressure of buffer gas is 1000-2000 Pa. With the new FALP [22] recombination rate coefficients as small as 5×10$^{-9}$ cm$^3$/s can be measured. To obtain very low partial pressures of hydrogen (densities down to 10$^{-11}$ cm$^{-3}$) the FALP and the gas handling systems were constructed with UHV technology. The plasma in the FALP is generated upstream by a microwave discharge in the flow of helium. Downstream from the discharge (~3 ms in time scale) Ar is added and in sequence of ion-molecule reactions Ar$^+$ dominated plasma is formed. Further downstream (~35 ms from the discharge) hydrogen is added and H$_3^+$ dominated plasma is formed. The measured velocity of the helium flow is used for conversion of the probe position to the decay time. In figures we arbitrarily use $t = 0$ at hydrogen inlet, upstream from this port $t < 0$ and downstream $t > 0$. The kinetics of formation and plasma decay is clear and can be calculated [16,23]. The time necessary for the transition from Ar$^+$ dominated plasma...
to $H_3^+$ dominated plasma depends on hydrogen partial density, $[H_2]$. The advantage of FALP over the AISA is that measurements are in continuous regime and hydrogen is added to already relaxed cold plasma with electron temperature ($T_e < 300$ K) given by the buffer gas temperature.

**Figure 1.** The FALP with long decay of afterglow plasma (not in scale). Indicated are the He input and the position of Ar and $H_2$ ports. The Langmuir probe is movable from the hydrogen port up to the end of the flow tube. The decay time in the range 0-60 ms is given by the position of the probe.

Fig. 2. shows the calculated plasma evolution along the flow tube. For the calculations we have deliberately used relatively high density of hydrogen ($[H_2] = 5 \times 10^{12}$ cm$^{-3}$). Below we will discuss the results of measurements at this particular density. Even if hydrogen density will be lower by factor of 20 (the formation will be longer by factor of 20) the plasma decay for $t > 10$ ms will be governed by the recombination of $H_3^+$ ions. This is because $Ar^+$ and $ArH^+$ recombine very slowly and $H_2^+$ recombines slowly in comparison with $H_3^+$ [24]. For study of the recombination of $H_3^+$ in the mixture with these ions it is enough if the relative density of $H_3^+$ is higher than 90%.

**Figure 2.** The calculated plasma formation and decay along the flow tube after the addition of Ar and $H_2$. In the right panel the detail of transition from $Ar^+$ dominated to $H_3^+$ dominated plasma after addition of hydrogen is shown.

### 3. Results

The examples of measured decreases of the electron density along the flow tube (“decay curves”) are plotted in the left panel of Fig. 3. The dependence of the decay rate on the hydrogen partial pressure is evident. The apparent recombination rate coefficients ($\alpha_{\text{eff}}$) were calculated from the electron density decays. In the data analyses the formation of $H_3^+$ dominated plasma was considered (see details in ref. [25]). For the comparison the decay curves obtained in AISA experiment are also shown in the right panel of Fig. 3. Without going into further details of the measurements we will discuss the results obtained in both FALP and AISA.
3.1. Dependence on the hydrogen partial pressure

Dependence of $\alpha_{\text{eff}}$ on the hydrogen partial density measured in the FALP experiment is plotted in Fig. 4. The dependence is similar to one obtained in AISA experiment.

The value of measured $\alpha_{\text{eff}}$ is increasing with $[\text{H}_2]$ (up to $[\text{H}_2] \sim 10^{12}$ cm$^{-3}$) and for higher densities of hydrogen (up to $[\text{H}_2] \sim 10^{14}$ cm$^{-3}$) the value of $\alpha_{\text{eff}}$ is constant. It is clear that the deionisation mechanism cannot be a pure binary dissociative recombination process. Because the conditions in the FALP are very well defined we can conclude, that the process of the recombination in the $\text{H}_3^+$ dominated low temperature plasma in He/Ar/H$_2$ mixture is a multicolisional process in which hydrogen molecules are involved. For even higher hydrogen densities, $[\text{H}_2] > 10^{14}$ cm$^{-3}$, we have observed further increase of $\alpha_{\text{eff}}$ but this is given by the formation of $\text{H}_5^+$ ions and their fast recombination. Using the FALP technique we have already studied the influence of $\text{H}_5^+$ formation on overall recombination process, for details see ref. [26]. We will see below that it is substantial to divide the measured dependence to the “low hydrogen density region” with $[\text{H}_2] \leq 10^{12}$ cm$^{-3}$ and to the “saturated region” with $2 \times 10^{12}$ cm$^{-3} \leq [\text{H}_2] \leq 1 \times 10^{14}$ cm$^{-3}$. In the low H$_2$ density region $\alpha_{\text{eff}}$ is increasing with $[\text{H}_2]$, in saturated region $\alpha_{\text{eff}}$ is constant independent on $[\text{H}_2]$.

3.2. Dependence on the temperature

Three body recombination processes, e.g. collision all radiative recombination (CRR) [27], have usually strong temperature dependence, $\alpha_{\text{CRR}} \sim T_e^{-4.5}$. Having indication of multicolisional character of the recombination process in low temperature plasma we measured the dependence of $\alpha_{\text{eff}}$ on the buffer
gas temperature. In this study we assume that decaying afterglow plasma is in thermodynamic equilibrium (or very close to equilibrium) with temperature given by buffer gas temperature (also discussion in accompanying paper by Plasil et al. [23]). The measurements of temperature dependence were carried out using the AISA [17]. When He density was kept nearly constant, the measured value of $\alpha_{\text{eff}}$ was decreasing with increasing buffer gas temperature. The observed dependence was very small, close to $\alpha_{\text{eff}} \sim T_e^{-0.5}$. An exponential factor was not 4.5 as it is expected for three body CRR recombination.

The form of the dependence on hydrogen density did not change with the temperature of the buffer gas. The dependencies of $\alpha_{\text{eff}}$ on hydrogen density measured at two different temperatures are plotted in Fig. 5. Note that the position of the transition to the saturated region is shifted at higher temperature towards higher $[\text{H}_2]$.

3.3. Dependence on the electron density
In our studies of $\text{H}_3^+$ recombination we have used three different experiments in several different configurations. In these experiments the electron density was varying over four orders of magnitude, from $n_e = 10^7$ up to $n_e = 5 \times 10^{11}$ cm$^{-3}$. When comparing obtained $\alpha_{\text{eff}}$ at fixed hydrogen density ([H$_2$] $\sim 10^{13}$ cm$^{-3}$) we cannot see substantial dependence on $n_e$. In the left panel of Fig. 6 the decay curves obtained in the different experiments are plotted. The differences between the decay curves are due to diffusion losses. The diffusion losses are considered in the data analyse.

![Figure 5](image5.png)

**Figure 5.** The temperature dependence of the effective recombination rate coefficient measured in AISA experiment.

![Figure 6](image6.png)

**Figure 6. Left panel:** The decay of $\text{H}_3^+$ dominated recombination-governed plasma. The used experimental techniques are indicated. In the insert the decay curve measured in TDT-CRDS is plotted. **Right panel:** log-log plot of the measured decay curves. The deviations from linearity at the end of the decays are due to diffusion losses. The diffusion losses are considered in the data analyse.
given by the differences in rates of diffusion losses, which are given by differences in pressures (from 200 to 1600 Pa) and diffusion lengths. If the plasma decay is governed by the recombination, then for electron density can be written: \( \frac{1}{n_{e}} = \frac{1}{n_{e0}} + \alpha_{\text{eff}} t \). In log-log scale for large \( t \), where \( \frac{1}{n_{e0}} \) can be neglected, we should obtain linear dependence: \( \ln(n_{e}) \sim (-\ln(t) - \ln(\alpha_{\text{eff}})) \). The values \( \ln(\alpha_{\text{eff}}) \) give the vertical shift. In the right panel of Fig. 6 there are such plots of the measured decay curves (at hydrogen density \([H_{2}] \sim 10^{13} \text{cm}^{-3}\)). As was already stated, we cannot see substantial dependence of \( \alpha_{\text{eff}} \) on electron density.

### 3.4. Dependence on the He density

The experimental conditions in the AISA and in the FALP differ in used pressures of the buffer gas. The obtained dependencies on hydrogen density measured at different pressures have similar shape but they differ in absolute value of the rate coefficients. The recombination rate coefficients measured in different experiments are in the Fig. 7 plotted versus helium buffer number density \([\text{He}]\). The values from “saturated region” are used in the plot, i.e. measured for \(2 \times 10^{12} \text{cm}^{-3} \leq [H_{2}] \leq 1 \times 10^{14} \text{cm}^{-3}\). The data obtained in previous studies using He/Ar/H\(_{2}\) afterglow are also included in the plot [28,29]. The binary recombination rate coefficients obtained in the storage ring experiments with the cold ion sources [8,9,10] and the value obtained in the theoretical calculation [11] is also indicated in the Fig. 7. The linear dependence on the helium density is obvious. The dependence can be expressed in the form: \( \alpha_{\text{eff}} = \alpha_{\text{eff} 0} + K_{\text{He}}[\text{He}] \), where \( K_{\text{He}} \) is constant given by the slope of the plot. The value obtained from the plot is \( K_{\text{He}}(260 \text{ K}) = 2.8 \times 10^{-25} \text{cm}^{6}\text{s}^{-1} \). The extrapolation for \([\text{He}] \rightarrow 0\) gives the value \( \alpha_{\text{eff}}(260 \text{ K}) = 7.5 \times 10^{8} \text{cm}^{3}\text{s}^{-1} \). The proposed mechanism of the multicollision recombination process is described in ref. [30] and will only shortly be described here.

![Figure 7](image)

**Figure 7.** The effective recombination rate coefficients measured in He/Ar/H\(_{2}\) afterglow experiments. The corresponding references are: Pittsburg - [28], Laube - [29]. The line is connecting just the points indicating data obtained by Pittsburg group and by Laube et al.

Calculations show [30] that at thermal energies in a collision of H\(_{3}^{+}\) with an electron highly excited neutral Rydberg molecule with lifetime 10-100 ps is formed. The collisions of these molecules with present He atoms are influencing the process of recombination in the plasma. These collisions can form long living highly excited molecular H\(_{3}^{*}\), which can autoionise or dissociate depending on the hydrogen partial density. If the density of H\(_{2}\) is small H\(_{3}^{*}\) autoionise and H\(_{3}^{+}\) are formed, the electron density then decays slowly. If the density of H\(_{2}\) is large (>2×10\(^{12}\) \text{cm}^{-3}) H\(_{3}^{*}\) dissociate in collisions with H\(_{2}\) and apparent recombination get faster. Assuming this process the linear dependence of \( \alpha_{\text{eff}} \) on \([\text{He}]\) can be obtained (for more details see [30]). Further studies on elucidation of role of H\(_{2}\) are in progress.
4. Conclusions
We studied recombination of $\text{H}_3^+$ ions in low temperature He/Ar/$\text{H}_2$ afterglow plasma in three different experiments, AISA, TDT CRDS and FALP. In all three experiments He was used as a buffer gas. From the measured recombination rate coefficient we obtained dependence on hydrogen partial pressure and on helium pressure. This clearly indicates, that the recombination of $\text{H}_3^+$ in afterglow plasma in He buffer is a multicolliisional multistep process.

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