Recombination studies in a He-Ar-H₂ plasma

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Abstract. The recombination of H⁺³ ions with electrons has been studied in afterglow plasma in three
different experiments. In two experiments, using the Variable Temperature Stationary Afterglow (VT-
AISA) and the Variable Temperature Flowing Afterglow (VT-FALP) techniques, a decay of the electron
number density was measured by an electrostatic Langmuir probe to determine the recombination rate
coefficient. In the third experiment a near infrared Cavity Ring-Down Absorption Spectrometer (CRDS)
was used to monitor the decay of the H⁺³ (v = 0) ion density during the afterglow. Measurements were
carried out in helium buffer gas with small admixtures of argon and hydrogen at total pressures ranging
from 150 up to 1200 Pa and at buffer gas temperatures ranging from 100 up to 330 K. In the experiments
the partial number density of hydrogen was varied from 5 × 10¹⁰ up to 1 × 10¹⁶ cm⁻³ and for this broad
range of hydrogen number densities effective recombination rate coefficients were obtained, which varied
over three orders of magnitude from 2 × 10⁻⁹ cm³s⁻¹ at [H₂] = 5 × 10¹⁰ cm⁻³ up to 3 × 10⁻⁶ cm³s⁻¹ at
[H₂] = 1 × 10¹⁶ cm⁻³. Using our experimental results we discuss possible mechanisms of recombination
in hydrogen plasma in a very broad range of several parameters: buffer gas pressure, temperature, electron
number density, hydrogen number density and internal excitation of recombining ions.

1. Introduction

Recombination of H⁺³ ions with electrons has been studied for fifty years both experimentally and
theoretically. In the recent five years this study was again very intensive because of new progress
in theory [1], new results from storage rings [2, 3] and also because of new results from plasma
experiments [4–6]. Because of the importance of H⁺³ in interstellar space and other hydrogen containing
plasmas we extended our studies of the recombination of this ion to lower temperatures. When speaking
about recombination of an ion with an electron we usually have in mind a binary interaction, which

© 2005 IOP Publishing Ltd 104
Journal of Physics: Conference Series 4 (2005) 104–110
doi:10.1088/1742-6596/4/1/014
Sixth International Conference on Dissociative Recombination
de-ionization we shall call recombination in plasma. This process is characterized by the recombination rate coefficient which, when obtained by integration of the cross section, is a function of the electron temperature only; in this integration the presence of neutral particles is not considered. To distinguish recombination rate coefficients obtained in afterglow experiments from those obtained by integration of the cross section, we will use the name effective recombination rate coefficient $\alpha_{\text{eff}}$ in plasma. The question is which parameters of the plasma will influence $\alpha_{\text{eff}}$ and how, if at all, this coefficient differs from the one obtained by integration of the cross section over a Maxwell distribution, $\langle v \sigma(v) \rangle$. Ideally, the recombination rate coefficient obtained by integration from the cross sections is a function of electron temperature only. In reality, in a beam experiment there is always the question about the internal energy of the colliding ions. Despite the simplicity of its structure, the $\text{H}_3^+$ ion is in this sense very difficult to study. Low temperature studies are even more complicated because of the existence of ortho and para states of $\text{H}_3^+$. 

In our previous studies of recombination in hydrogen plasma we observed a dependence of the recombination rate coefficient $\alpha_{\text{eff}}$ on the partial pressure of hydrogen. The dependence is similar to the one observed for rate coefficients of ternary ion-molecule association reactions [7]. If indications of ternary processes are observed also in the recombination of $\text{H}_3^+$ ions with electrons, we can, in analogy with ternary ion-molecule association reactions, expect an enhanced temperature dependence of this process. The precise measurement of the temperature dependence of $\alpha_{\text{eff}}$ at low hydrogen number densities, where the influence of $\text{H}_5^+$ formation is negligible, was the main aim of the studies reported here.

2. Experiment

The experimental set-up used was described already several times [4], so only a short description will be given here. We use a stationary afterglow (SA) experiment with a large discharge vessel to suppress diffusion and prolong the decay of the plasma, which allows slow recombination processes to be studied. The vacuum chamber is built with UHV technology to minimize the influence of impurities on the decay of the plasma. The purity of the gas during the discharge is better than 0.1 ppm. The main part of the instrument consists of a stainless-steel cylinder 40 cm in diameter and 40 cm long. The chamber is equipped with a mass spectrometer and a cylindrical Langmuir probe to measure the ionic composition and the electron number density, respectively. A plasma is generated by pulses of microwaves produced by an external magnetron and entering the chamber via a quartz window (see figure 1).

The discharge chamber has two envelopes for cooling with liquid nitrogen and for thermal insulation (see figure 1). The temperature of the chamber is monitored by several thermocouples. The plasma is

![Figure 1. Schematic view of the Advanced Integrated Stationary Afterglow (AISA) instrument. The pulse of microwaves from an external magnetron enters the discharge chamber via a quartz window. The evolution of the electron number density is measured by a Langmuir probe, time resolved mass spectra are obtained using a differentially pumped mass spectrometer.](image-url)
generated in helium with small admixtures of argon and hydrogen. The kinetics of the formation of H$_3^+$ ions were studied in our previous work [4]; they are well understood so we will describe them only briefly here. Considering a mixture of 99% He, 0.8% Ar and 0.1% H$_2$ at an overall pressure of 200 Pa, predominantly He$^+$ and Ar$^+$ will be produced in the microwave pulse. Within few milliseconds He$^+$ will be converted in ternary association to He$_2^+$, which in presence of Ar forms Ar$^+$. The remaining and the just formed Ar$^+$ reacts with H$_2$, and in a sequence of ion-molecule reactions ArH$^+$, H$_3^+$ and finally H$_5^+$ ions are formed. H$_3^+$ ions react not at all with He and only very slowly, in ternary reactions, with H$_2$ or Ar, forming H$_5^+$ or ArH$_3^+$, respectively. We studied the formation and recombination of H$_3^+$, but we used partial pressures of Ar as low that the presence of ArH$_3^+$ and its influence on the overall recombination process can be neglected. At various hydrogen number densities we measured the dependence of the effective recombination rate coefficient on the partial pressure (i.e., the partial flow rate) of argon. Examples of the dependencies obtained are plotted in figure 2. From these plots we can conclude that the influence of Ar on the measured effective recombination rate coefficient can be neglected if the flow rate of Ar is below 0.5 sccm (standard cubic centimeters per minute). This flow is sufficient for fast formation of H$_3^+$, so we have used it in the present experiments. Since association reactions are faster at lower temperatures, it is expected that also the influence of Ar is more pronounced at lower temperatures, as confirmed by the data plotted in figure 2.

3. Data analysis

In our previous studies [7] we have found that at hydrogen number densities below 5 × 10$^{13}$ cm$^{-3}$, H$_3^+$ ions are the dominant ions in the afterglow and the influence of the formation of H$_3^+$ can be neglected even at temperatures as low as 130 K. The balance equation can (using the assumption of quasineutrality) be written in the form

$$\frac{dn_e}{dt} = -\alpha_{\text{eff}} [\text{H}_3^+] n_e - \nu_D n_e - \nu_R n_e = -\alpha_{\text{eff}} n_e^2 - \nu_D n_e - \nu_R n_e$$

(1)

where $n_e$ is the electron number density, the second term represents diffusion losses and the third term eventual reactive losses. When diffusion and reactive losses can be neglected, this equation has a simple solution: $1/n_e = 1/n_{e0} + \alpha_{\text{eff}} t$. A plot of $1/n_e$ versus $t$ should then be linear with a slope given by the recombination rate coefficient $\alpha_{\text{eff}}$. This simple solution is often used for analysis of the decay curves of recombination dominated plasmas. If diffusion and reactive losses cannot be simply neglected, it is more convenient to write the balance equation in the form (the derivative $dn_e/dt$ written as $n'_e$)

$$-n'_e/n_e^2 = \alpha_{\text{eff}} + \nu_D/n_e + \nu_R/n_e \quad \text{or} \quad (-n'_e/n_e^2 - \nu_D/n_e) = \alpha_{\text{eff}} - \nu_R/n_e$$

(2)
Figure 3. Example of data measured in an AISA experiment at 150 K, helium pressure 160 Pa and several partial pressures of hydrogen. Upper panel: Evolution of the electron number density during the afterglow. Lower panel: Reciprocal plot of \( 1/n_e \) versus time.

Here, a plot of \( n'_e/n_e^2 \) versus \( 1/n_e \) should be linear with the slope given by the diffusion losses and the ordinate axis intercept yielding \( \alpha_{\text{eff}} \). When the diffusion losses can be estimated by measurements or calculations then also a plot of \( (-n'_e/n_e^2 - \nu_D/n_e) \) versus \( 1/n_e \) yields the value of \( \alpha_{\text{eff}} \). The data analysis using this type of plots we will call advanced analysis.

4. Results and discussion

The reported recombination studies were carried out at different temperatures ranging from 130 to 230 K. At a given temperature the hydrogen number density was varied in the range from \( 1 \times 10^{11} \) up to \( 3 \times 10^{13} \) cm\(^{-3} \). These measurements are covering the region where a strong dependence of the recombination rate on the hydrogen partial pressure was observed in our previous studies [4, 7]. In figure 3 the decay curves obtained at 150 K and several hydrogen number densities are plotted together with reciprocal plots of \( 1/n_e \) versus time. Already from these plots it is evident that the recombination rate strongly depends on the hydrogen number density.

In figure 4 the same data are replotted as the dependence of \( (-n'_e/n_e^2 - \nu_D/n_e) \) on \( 1/n_e \). In the advanced analysis the fast slope at early afterglow (small values of \( 1/n_e \)) corresponds to the formation of a \( \text{H}_3^+ \) dominated plasma. The plasma contains slowly recombining ions (\( \text{He}^+, \text{Ar}^+, \text{ArH}^+ \)) during this time. The linear parts of the curves correspond to the decay of plasmas with constant recombination rate coefficients. An advantage of the advanced analysis is that determination of \( \alpha_{\text{eff}} \) is independent of diffusion and of reactive losses, as long as the corresponding terms in the balance equation are linear. We also carried out several sets of measurements where the hydrogen number density was kept constant and the temperature was changed. An example of advanced analysis decay curves obtained in such a series are plotted in figure 5.

In parallel to the measurements we also modelled the plasma formation to obtain the evolution of the plasma composition during the early afterglow and during the recombination dominated afterglow (see [4] for details). The \( \text{H}_3^+ \) rate coefficients were then calculated from the parts of the decay curves where \( \text{H}_3^+ \) are found to be the dominant ions. In figure 6 these recombination rate coefficients \( \alpha_{\text{eff}} \), obtained at different temperatures, are plotted as a function of the hydrogen number density.

Two aspects have to be noted regarding the data plotted in figure 6. First, the shape of the dependence
Figure 4. The same data as shown in figure 3; advanced analysis of the decay of the H$^+_3$ dominated plasma. The intersections of the dashed lines with the vertical axis give $\alpha_{\text{eff}}$.

Figure 5. Example of AISA data measured at [H$_2$] = 10$^{12}$ cm$^{-3}$ for $T$ = 130 and 230 K.

Figure 6. Effective recombination rate coefficients $\alpha_{\text{eff}}$ for H$_3^+$ measured in AISA experiments.

of $\alpha_{\text{eff}}$ on [H$_2$] is independent of the temperature; it is the same for low temperature (130 K) and for high temperature (230 K). Second, the measured $\alpha_{\text{eff}}$ increases for decreasing temperature in the whole range of hydrogen number densities covered. Despite the large scatter of the data this general feature is obvious. This observation is in agreement with recent storage ring data where as a general trend the measured rate coefficient increases with decreasing electron temperature. The accuracy of the absolute scale of $\alpha_{\text{eff}}$ is given by a calibration of the Langmuir probe using recombination of O$_2^+$ with electrons; we expect this to be better than ±30%. The initial electron number densities are of the order of $n_e \sim 10^{10}$ cm$^{-3}$, so $\alpha_{\text{eff}}$ is obtained from the decay between $n_e \sim 10^{10}$ and $n_e \sim 10^8$ cm$^{-3}$ (see figure 3). We calculated the rate coefficient of collision radiative recombination (CRR) at these number densities for 130 K and found that
Recently we studied the recombination of $\text{H}_3^+$ using three different afterglow experiments: the already mentioned AISA (see also [4, 5]), the Flowing Afterglow (FALP) [7] and the Stationary Afterglow (Test Tube) using IR absorption (CRDS) for measuring the time evolution of the ion number density $[\text{H}_3^+ (v = 0)]$ [8, 9]. In all three experiments He/Ar/$\text{H}_2$ mixtures were used for formation of a $\text{H}_3^+$ dominated afterglow. The plasmas in these three experiments have very different parameters and very different initial plasma densities. Therefore, the decay of the recombination dominated plasma has different characteristic decay times. Figure 7 shows examples of decay curves obtained in AISA, FALP and Test Tube experiments. The log-log representation demonstrates the range of plasma densities and time scales covered by the experiments. The dashed line indicates a decay $1/n_e \sim \alpha_{\text{eff}} t$ with $\alpha_{\text{eff}} = 1.37 \times 10^{-7} \text{ cm}^3\text{s}^{-1}$. Obviously, the obtained $\alpha_{\text{eff}}$ is independent of the initial plasma density and of the time of formation of the $\text{H}_3^+$ dominated plasma.

The plotted data were taken at slightly different buffer gas temperatures, producing small shifts among the data from different experiments. The actual temperature dependence can be seen from the results for $\alpha_{\text{eff}}$ plotted in figure 8. Here, data obtained using all three techniques during the years 2000–2004 are plotted. We stress that for AISA and FALP the electron number densities are measured by a Langmuir probe, while in the Test Tube experiments the ion number density is measured by IR absorption CRDS. From the Test Tube studies only lines fitted through the measured points together with “low pressure limits” (giving values not influenced by formation of $\text{H}_5^+$) are plotted.

As demonstrated in our previous papers [7] and in an accompanying paper in this volume [10], the increase of $\alpha_{\text{eff}}$ at $[\text{H}_2] > 6 \times 10^{14} \text{ cm}^{-3}$ (dependent on temperature and pressures of He and $\text{H}_2$) can be explained by formation of $\text{H}_5^+$ ions. Dependent on the actual conditions of the experiment a steady state approximation or the assumption of thermodynamic equilibrium can be used to calculate the increase due to this channel. For $[\text{H}_2] < 10^{13} \text{ cm}^{-3}$, the formation of $\text{H}_5^+$ can be neglected. In the region where $\alpha_{\text{eff}}$ is independent of $[\text{H}_2]$ we obtained a dependence of $\alpha_{\text{eff}}$ on temperature; in accordance with previous studies by Leu et al. [11] and Amano [12], our data also suggest a $T^{-1}$ dependence in the region 100–330 K. Because of the dependence of $\alpha_{\text{eff}}$ on $[\text{H}_2]$ at low hydrogen densities, we have to assume that the observed recombination process is a ternary process where a $\text{H}_3^+$ ion, an electron and a $\text{H}_2$ molecule are involved. Having in mind that we cannot change the He pressure substantially in these experiments, we also cannot exclude an influence of He in this process.
Figure 8. Dependence of $\alpha_{\text{eff}}$ for the recombination of $\text{H}_3^+$ ions with electrons on hydrogen number density and temperature as observed in the afterglow experiments AISA, FALP and Test Tube – CRDS. The measurements were carried out in a $\text{H}_3^+$ dominated plasma created in a He/Ar/H$_2$ mixture. The pressures of the buffer gas (He) are indicated.

A new FALP experiment is currently in preparation, which will cover the low hydrogen-density region up to now accessible only in the AISA experiment. At this moment we can only speculate on the actual mechanism observed. Further studies are required to explain the observations presented here and to put them in the context of storage ring results and theory.

Acknowledgments

Thanks for financial support are due to GACR (205/02/0610, 202/02/0948, 202/03/H162), GAUK-278/2004/B-FYZ/MFF, and MSM 113200002. The experiments were carried out with support from EC's RTN under contract HPRN-CT-2000-0142 ETR, VEGA 1/1016/04.

References

[1] Kokoouline V, Greene C H 2003 Phys. Rev. A 68 012703
[2] McCall B J et al. 2003 Nature 422 500
[3] Wolf A et al. 2004 Physica Scripta T110 193–9
[4] Plašil R, Glosík J, Poterya V, Kudrna P, Rusz J, Tichy M and Pysanenko A 2002 Int. J. Mass Spectrom. 218 105–30
[5] Glosík J, Plašil R, Poterya V, Kudrna P, Tichy M 2000 Chem. Phys. Lett. 331 209
[6] Poterya V, Glosík J, Plašil R, Tichy M, Kudrna P, Pysanenko A 2002 Phys. Rev. Lett. 88 044802
[7] Glosík J, Novotný O, Pysanenko A, Zakouřil P, Plašil R, Kudrna P, Poterya V 2003 Plasma Source Sci. Technol. 12 S117
[8] Macko P, Báno G, Hlavenka P, Plašil R, Poterya V, Pysanenko A, Votava O, Johnsen R and Glosík J 2004 Int. J. Mass Spectr. 233 299–304
[9] Macko P, Plašil R, Kudrna P, Hlavenka P, Poterya V, Pysanenko A, Báno G and Glosík J 2002 Czech. J. Phys. 52 D695–D704
[10] Plašil R, Hlavenka P, Macko P, Báno G, Pysanenko A and Glosík J 2005 J. Phys.: Conf. Series this volume
[11] Leu MT, Biondi MA and Johnsen R 1973 Phys. Rev. A 8 413
[12] Amano T 1990 J. Chem. Phys. 92 6492–501