The recombination of spectroscopically identified $\text{H}_3^+(v=0)$ ions with electrons

R Plašil,1 P Hlavenka,1 P Macko,2 G Báňo,3 A Pysanenko1 and J Glosík1

1 Charles University Prague, Mathematics and Physics Faculty, Department of Electronics and Vacuum Physics, V Holesovičkách 2, Prague 8, Czech Republic
2 Comenius University, Department of Plasma Physics, Bratislava, Slovak Republic
3 Research Institute for Solid State Physics and Optics, HAS, Budapest, Hungary

E-mail: radek.plasil@mff.cuni.cz

Abstract. We report a study of the recombination of $\text{H}_3^+(v=0)$ ions with thermal electrons at 330 and 100 K. A near infrared cavity ring-down absorption spectrometer (CRDS) working on the $\nu_2 = 3 \leftarrow 0$ transition of $\text{H}_3^+$ ($\lambda = 1382$ nm) has been used to monitor the $\text{H}_3^+$ $(v=0)$ ion number density in decaying afterglow plasma. The plasma was created in helium gas with small admixtures of argon and hydrogen by pulses of microwaves. The measurements were carried out for hydrogen number densities ranging from $10^{13}$ up to $10^{16}$ cm$^{-3}$. The total pressure in the discharge tube was 4–10 mbar. The temperature of the recombining ions was determined from the Doppler broadening of absorption lines. The obtained effective recombination rate coefficients are $\alpha(\text{H}_3^+(v=0)) = (0.8 \pm 0.3) \times 10^{-7}$ cm$^3$s$^{-1}$ and $\alpha(\text{H}_3^+(v=0)) = (2.3 \pm 1.1) \times 10^{-7}$ cm$^3$s$^{-1}$ at 330 and 100 K, respectively. The influence of the formation of $\text{H}_5^+$ at higher pressures and lower temperature is also discussed.

1. Introduction

Several plasma techniques are available for studies of ion recombination with electrons. Typically the decay of a plasma in which a certain type of ions dominates is monitored and from the measured decay curves the rate coefficients are extracted in such experiments. Stationary and flowing afterglow techniques are the most common examples, where the plasma decay is monitored in time and in space, respectively. In the majority of these experiments electron number densities are measured (by Langmuir probes or microwave techniques) and recombination rate coefficients are calculated under the assumption of quasineutrality. Only in few experiments the ion density was measured directly using ion spectroscopy techniques [1]. The reason is that typical ion number densities in low temperature plasma used for afterglow studies are very low (order of $10^8$–$10^{11}$ cm$^{-3}$); this is sufficient for electron density measurements but only in very special cases such low densities of ions can be measured directly. The anomaly of the recombination of the $\text{H}_3^+$ ion [2] and discrepancies among results obtained from different experiments are the reasons to try to measure the ion number density directly and possibly also the temperature of the recombining ions during the afterglow. Cavity ring-down spectroscopy (CRDS) is a very suitable technique for such afterglow studies. It allows state specific density measurements, with identified vibrational and rotational level of the ions, and, at the same time, the kinetic energy of the ions can be determined from the Doppler broadening of the absorption lines. CRDS measures the absolute ion density as needed in recombination studies. On the other hand certain limitations of the CRDS technique arise from the fact that only a single quantum state of the ion is probed and therefore one has to assume...
argon and hydrogen. A typical mixture composition has been as follows: \([\text{He}] = 3 \times 10^{17} \text{ cm}^{-3}\) and \([\text{Ar}] = 1 \times 10^{13} \text{ cm}^{-3}\). To obtain the dependence of the recombination rate on the hydrogen number density the flow rate of hydrogen was varied from \(10^{13}\) up to \(10^{16} \text{ cm}^{-3}\). The total pressure in the discharge tube was 4–10 mbar. The number density of \(\text{H}_3^+\) ions, as will be discussed in some detail later.

2. Experiment

Cavity ring-down spectroscopy (CRDS) is used in this experiment to measure the time-resolved \(\text{H}_3^+\) densities in stationary afterglow. Figure 1 shows a schematic diagram of the apparatus. It consists of a glass discharge tube of 4 cm diameter, in which the pulsed plasma was generated. The plasma was generated either by a microwave generator connected to a waveguide (\(\sim 0.5\) ms pulse length, \(\sim 250\) Hz repetition frequency) or by a magnetron coupled to large microwave cavity (\(\sim 0.5\) ms pulse length, 50 Hz repetition frequency). A fast high voltage switch with a rise time of the order of a few microseconds was used to control the magnetron voltage. The use of the large microwave cavity has the advantage of generating a longer plasma column (\(\sim 30\) cm in the cavity versus \(\sim 7\) cm in the waveguide) that enables to measure lower \(\text{H}_3^+\) densities. On the other hand, because of better plasma adjustment the ion density is higher in the waveguide (\(5 \times 10^{11} \text{ cm}^{-3}\) versus \(5 \times 10^{10} \text{ cm}^{-3}\) in the large microwave cavity).

The buffer gas flowing through the discharge tube consisted of helium with small admixtures of argon and hydrogen. A typical mixture composition has been as follows: \([\text{He}] = 3 \times 10^{17} \text{ cm}^{-3}\) and \([\text{Ar}] = 1 \times 10^{13} \text{ cm}^{-3}\). To obtain the dependence of the recombination rate on the hydrogen number density the flow rate of hydrogen was varied from \(10^{13}\) up to \(10^{16} \text{ cm}^{-3}\). The total pressure in the discharge tube was 4–10 mbar. The number density of \(\text{H}_3^+\) ions, necessary for calculation of the recombination rate coefficient, was measured by CRDS on the \(v_2 = 3 \rightarrow 0\) transition of \(\text{H}_3^+\) around the wavelength of 1380 nm. CRDS, first demonstrated by O’Keefe and Deacon [3], is based on the observation of the ring-down decay rate of an injected laser beam stored in a cavity comprised of ultra-high reflective spherical mirrors.

Figure 1. Schematic diagram of the apparatus. Highly reflective mirrors used for CRDS are mounted on both ends of the discharge tube. The microwave waveguide (a) was used to generate plasma in the discharge tube. It can be substituted by a plasma generator with large microwave cavity (b). In the second case the discharge tube can be cooled by liquid \(\text{N}_2\). The buffer gas was flowing in the direction from the mirrors towards the discharge to prevent plasma enhanced deposition and destruction of the mirrors.
meters. For our measurements, we used an alternative approach that employs continuous wave (cw) laser sources using the transition intensities calculated by Neale et al. [4]. This approach was first proposed by Lehmann in 1996 [5] and followed by Romanini et al. [6,7]. Figure 2 illustrates the concept of cw-CRDS. The physical principles are described in the mentioned references and can also be found in our earlier papers [8–10].

Briefly, a single mode diode laser tunable by an external resonator is used. The laser beam passes through an optical isolator with backward isolation of 35 dB, followed by an acousto-optic switch (AOS). The AOS is used to interrupt the cavity injection once the build-up in the ring-down cavity occurs. It allows obtaining clean ring-down decays. After passing through the AOS, the mode 1 of the AOS is matched by a spatial filter to the TEM00 mode of the ring-down cavity. The cavity output is focused by a single lens to an InGaAs avalanche photodiode. The cavity mirrors (radius 1 m) are mounted on tilt stages. One stage includes a piezoelectric tube for modulating the cavity length. Two detection approaches are possible. Either the cavity length is modulated by slightly more than \(\lambda/2\), thus producing a passage through resonance with the laser wavelength twice per modulation period. Or alternatively, a tracking circuit is used that modulates the cavity length around the resonance length and, at the same time, adjusts the offset of modulation to maintain the resonance events in the middle of the modulation range. By using this circuit, the maximum ring-down repetition rate is about 300 Hz. The ring-down decay signal is digitized by a 14 bit/2 MHz PC card. The wavelength of the laser line was measured online by a \(\lambda\)-meter and the laser tuning was monitored by a Fabry-Perot etalon of 1 GHz free spectral range. To avoid plasma-enhanced deposits on the mirrors, the inlets of the He buffer gas are located close to the mirrors so gas is flowing from the mirrors towards the discharge region.

2.1. \(H_3^+\) line positions

Prior to the measurements of the \(H_3^+\) decay in pulsed discharge mode, we worked in continuous mode in order to assign the absorption spectrum of \(H_3^+\). The most intense absorption line is shown in figure 3. The wavenumber scale in this figure (horizontal axis) was linearized by using fringes of the etalon and absolutely calibrated using the accurate value for the water line visible next to the \(H_3^+\) line. We estimate the accuracy of the \(H_3^+\) line frequency measurement to be 0.015 cm\(^{-1}\). The scale of the absorption coefficient (vertical axis) of the water lines is different from that of the \(H_3^+\) line because the absorption column of \(H_3^+\) was only about 7 cm while residual water vapor was along the whole cavity (length 71 cm). The integrated area of the water line gives an \(H_2O\) partial pressure of 1.4 mPa, that is \(10^{-6}\) in comparison with the total pressure. This shows the high purity of the gases used and of the vacuum system.
2.2. Temperature evolution during the afterglow

The key parameter necessary for the description of a plasma is the plasma temperature. In non thermal plasmas it has to be replaced by a combination of ion and electron temperature, particularly for describing the role of recombination in the plasma. For this reason the temperature dependencies of specific rate coefficients are of particular interest in the studies of the elementary plasma processes. For the description of an \( \text{H}_3^+ \) dominated plasma the temperature dependence of the recombination rate coefficient has to be determined, thus we need to measure the actual temperature of the decaying plasma. For simplicity we will assume here that the plasma is close to thermodynamic equilibrium during its decay, meaning that all components (ions, electrons and neutrals) can be characterized by the same temperature. In such a case it is sufficient to measure the temperature of one of these components.

In the present experiments we are using the Doppler broadening of the spectral lines to measure the temperature. We are using different approaches to determine the plasma temperature in low and high temperature experiments, respectively. In experiments with the large microwave cavity at 330 K, when the discharge column length is almost half of the cell length, we used the strongest water line at 7243.012 cm\(^{-1}\) and measured the evolution of its profile during the decay of the plasma. By fitting the water line at different decay times with a Gauss function we obtained the evolution of its Doppler width. From this data the variation of temperature during the afterglow was obtained, as shown in figure 4. Note that immediately after the microwave pulse the temperature was about 340 K and the temperature is decreasing within 0.5 ms to 325 K, corresponding to the temperature of the discharge tube.

---

**Figure 3.** Example of an \( \text{H}_3^+ \) absorption line measured in continuous discharge using cw-CRDS. From the line profile the indicated ion temperature was calculated. The observed \( \text{H}_2\text{O} \) absorption line was used to improve the accuracy of the absorption frequency measurements of this \( \text{H}_3^+ \) line. The thin line represents the calculated \( \text{H}_2\text{O} \) spectrum in the measured interval.

---

**Figure 4.** Example of the gas temperature evolution during the afterglow as determined from the Doppler broadened \( \text{H}_2\text{O} \) absorption line at 7243.012 cm\(^{-1}\). The insert shows an example of the line profile measured at decay time \( \sim 0.7 \) ms. The vertical dashed line indicates the position of this profile in time.
Figure 5. Example of the measured \( \text{H}_3^+ \) density decay and kinetic temperature evolution during the afterglow as determined from the width of the \( \text{H}_3^+ \) absorption line \( \nu_2 = 3 \leftarrow 0 \) R(1,0) at 7241.260 \( \text{cm}^{-1} \). Note the different time scales used in the upper and in the lower panel. The insert shows an example of the line profile measured at 0.15 ms.

Wall. The temperature determined from the measurements of the \( \text{H}_3^+ \) line width during the afterglow gives approximately the same values, however with larger errors due to the weaker line amplitude.

At \( \sim 100 \text{ K} \), when the discharge tube walls were cooled with liquid nitrogen, the gas temperature could not be determined from the Doppler width of water line since all residual water molecules had been trapped on the tube wall. In this case, it was necessary to use the evolution of the \( \text{H}_3^+ \) line width to measure the plasma temperature during the afterglow; an example of this data is given in figure 5.

There are three plots included in the figure: The evolution of the \( \text{H}_3^+ \) ion number density during the afterglow, the evolution of the ion temperature, and (in the insert) an example of the measured line profile corresponding to a decay time of 0.15 ms. Note that the upper and lower plots have different time scales. The temperature was measured just during the early afterglow (up to 0.6 ms in the plot) when the plasma density is high enough to obtain a reliable absorption signal and a corresponding absorption line. From the data plotted in the lower panel it is obvious that during the early afterglow, which is dominated by recombination, the temperature of the plasma is about 105 K. The discharge tube was cooled by liquid nitrogen in these measurements so the actual temperature of the discharge tube was close to 73 K.

3. Data analysis, results and discussion

If recombination and diffusion are the dominant processes in decaying hydrogen plasma the balance equation can be written in the form

\[
\frac{dn_e}{dt} = -\alpha_3 [\text{H}_3^+] n_e - \alpha_5 [\text{H}_5^+] n_e - n_e/\tau. \tag{1}
\]

Here we already considered that \( \text{H}_3^+ \) and \( \text{H}_5^+ \) ions, with different rates of recombination, are present in the decaying plasma. Diffusion losses are introduced by the last term. If the ion number density is measured in the experiment, the balance equation has to be rewritten using the measured quantity, in our case the \( \text{H}_3^+ \) number density \( [\text{H}_3^+] \). Under the assumption of quasineutrality and using \( R = [\text{H}_5^+]/[\text{H}_3^+] \), we obtain

\[
\frac{d[\text{H}_3^+]}{dt} = -\frac{\alpha_3 + R\alpha_5}{\alpha_{\text{CRDS}}} [\text{H}_3^+]^2 - [\text{H}_3^+] /\tau = -\alpha_{\text{CRDS}} [\text{H}_3^+]^2 - [\text{H}_3^+] /\tau \tag{2}
\]

An effective recombination rate coefficient \( \alpha_{\text{CRDS}}^{\text{eff}} = \alpha_3 + R\alpha_5 \) can be introduced in this kind of differential equation. Furthermore, if \( R \) is constant during the decay, the solution of this differential
equation can be expressed analytically. Under conditions where diffusion can be neglected the analytical solution yields a proportionality of $1/[\text{H}_3^+]$ to the decay time, as is the case for recombination in plasma with only a single type of ions. An example of the obtained dependencies of $[\text{H}_3^+]$ and $1/[\text{H}_3^+]$ on the decay time is plotted in figure 6. The accurate value of $\alpha_{\text{CRDS eff}}$ can be obtained by fitting the data with a function considering both recombination and diffusion losses.

The measurements were carried out using several transitions in the second overtone band of $[\text{H}_3^+]$. The observed transitions, some of which were used for the recombination studies, are plotted in figure 7. Naming convention and frequencies are taken from [11].
The initial plasma density (number density of \([H^+3]\)) varied over two orders of magnitude from \(5 \times 10^9\) to \(5 \times 10^{11} \text{ cm}^{-3}\). We were able to monitor the decay of \([H^+3]\) over one order of magnitude, so depending on the initial number density the decay time varied from \(\sim 0.3\) up to \(\sim 3\) ms, with shorter decay time corresponding to higher initial density and vice versa. We did not observe any correlation between the initial conditions and the obtained recombination rate.

Recombination rate coefficients obtained in the present study are plotted in figure 8 as a function of the hydrogen number density, together with data obtained previously in AISA experiments [12]. The particular transitions used to obtain the recombination rate coefficient are indicated. We should stress here that the AISA data were obtained by measuring the electron number density using a Langmuir probe without identification of the internal ion state, the ions were identified only by a mass spectrometer (see the paper of Glosík et al. in this volume). The main benefit of the use of CRDS in the present work is the determination of the \(H^+_3\) recombination rate from a direct measurement of the \(H^+_3\) density.

From the plotted \(\alpha_{\text{CRDS}}^{\text{eff}}\) we can clearly see increase of the obtained values with increasing hydrogen number density, which is related to the already discussed relation \(\alpha_{\text{eff}}^{\text{CRDS}} = \alpha_3 + R \alpha_5\) and the proportionality of \(R\) to \([H_2]\). The term proportional to \(R\) is expressing the influence of rapidly recombining \(H^+_5\) ions on the plasma decay. Under certain experimental conditions the actual value of the ratio \(R\) depends on \(n_e, [H_2], [He]\) and temperature. For the conditions of the present experiment at 100 K the second term is represented by the dashed line in figure 8. The term \(R \alpha_5\) can be neglected for \([H_2] < 3 \times 10^{13} \text{ cm}^{-3}\), but has to be taken into account for higher \(H_2\) concentrations. The formation of \(H^+_5\) is slow at higher temperatures and its influence is playing a role only at higher \([H_2]\) densities, which is enhancing the formation of \(H^+_5\) ions. If the plasma is in thermodynamic equilibrium the ratio \(R\) can be calculated for given temperature and partial pressures of helium and hydrogen. From the measured dependence of \(\alpha_{\text{eff}}^{\text{CRDS}}\) on \([H_2]\) the values of \(\alpha_3\) and \(\alpha_5\) can then be obtained.

**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 1132000002. The experiments were carried out with support from EC’s RTN under contract HPRN-CT-2000-0142 ETR, VEGA 1/1016/04 and with support from Euroatom.
References

[1] Amano T 1990 J. Chem. Phys. 92 6492
[2] Kokoouline V and Greene C H 2003 Physical Review A 68 01 2703
[3] O’Keeffe A and Deacon D A G 1988 Rev. Sci. Instrum. 59 2544
[4] Neale L, Miller S and Tennyson J 1996 Astrophys. J. 464 516–520
[5] Lehmann K K 1996 Ring-down cavity spectroscopy cell using continuous wave excitation for trace species detection US patent no. 5,528,040
[6] Romanini D, Kachanov A A, Sadeghi N and Stoeckel F 1997 Chem. Phys. Lett. 264 316–22
[7] Romanini D, Kachanov A A and Stoeckel F 1997 Chem. Phys. Lett. 270 538–45
[8] Macko P, Plašil R, Kudrna P, Poterya V, Pysanenko A, Báňo G and Glosík J 2002 Czech. J. Phys. 52 D695–D704
[9] Macko P, Bánó G, Hlavenka P, Plašil R, Poterya V, Pysanenko A, Votava O, Johansen R and Glosík J 2004 Int. J. Mass Spectr. 233 299–304
[10] Macko P, Bánó G, Hlavenka P, Plašil R, Poterya V, Pysanenko A, Dryahina K, Votava O and Glosík J 2004 Acta Physica Slovaca 54 263–71
[11] Lindsay C M and McCall B J 2001 Journal of Molecular Spectroscopy 210 60–83
[12] Plašil R, Glosík J, Poterya V, Kudrna P, Rusz J, Tichý M and Pysanenko A 2002 Int. J. Mass Spectrom 218 105–30