Study of Collisional-radiative Recombination Using CRYO-FALP

S. Opanasiuk, T. Kotrík, P. Dohnal, M. Hejduk, P. Rubovič, R. Plašil, and J. Glosík
Charles University in Prague, Faculty of Mathematics and Physics, Prague, Czech Republic.

Abstract. In the article the description of CRYO-FALP apparatus and physical processes that are relevant to the study of collisional-radiative recombination are described. Brief history and some details of the afterglow experiments are also given. Also it is discussed the determination of electron temperature by monitoring diffusion losses during the afterglow.

Introduction

Collision radiative recombination (CRR) is a very important process in low temperature high density plasmas, but up to now only limited number of experimental investigations of this process has been carried out at temperatures below 300 K. The process was first discussed in [Bates et al., 1962], where a statistical theory was presented to describe radiative and collisional processes. Later, it have been studied experimentally by various authors, such as [Tsuji, 2002] and [Skrzypkowski, 2004].

The CRR process can be defined by the formula:

\[ A^+ + e^- + e^- \rightarrow A + e^- \quad (1) \]

It was found that if the temperature of plasma is sufficiently low, radiative stabilization dominates and if electron density is high, collisional stabilization dominates in the process. The universal formula for the calculation of the recombination rate coefficient was given in [Stevefelt et al., 1975]:

\[ \alpha_{\text{CRR}} = 3.8 \times 10^{-9} T_e^{-4.5} n_e + 1.55 \times 10^{-10} T_e^{-0.63} + 6 \times 10^{-9} T_e^{-2.18} n_e^{0.37} \quad [\text{cm}^3/\text{s}], \quad (2) \]

where \( \alpha_{\text{CRR}} \) is recombination rate coefficient, \( T_e \) is the electron temperature (in Kelvin) and \( n_e \) is electron density (in cm\(^{-3}\)). The formula is based on the earlier works [Bates et al., 1962] and [Mansbach and Keck, 1969] and then reviewed in several publications, such as [Flannery, 1994], [Massey and Gilbody, 1974]. We use \( T_e \) in agreement with Stevelfelt formula for afterglow plasma in thermodynamic equilibrium, so \( T_e = T_{\text{gas}} = T_{\text{ion}} = T \). The first term in the formula (2) accounts collisional recombination. It is proportional to the electron density and depends on the electron temperature. The second term describes radiative recombination component and it is independent on the electron density. The last term, which was introduced in [Stevefelt, 1975], is a competition between collisional and radiative processes. The formula was confirmed experimentally for the high temperatures in the works by several authors ([McDaniel, 1993], [Pert, 1990], [Bianditi, 1975] etc.).

For over 40 years, flowing afterglow (FA) has been a leading technique for study of elementary processes in thermal and near thermal plasmas. It was developed by Ferguson [Ferguson, 1964] in the early sixties. Initially it was built for the study of ion-molecule reactions, but then the sphere of application of FA technique was expanded to the study of different types of recombination. Nowadays it is a very versatile tool for ion kinetics studies in plasma physics and chemistry.

Different modifications of FA are used for particular studies. Langmuir probe (to monitor plasma decay along the flow tube) can be added to FA apparatus to study recombination and relaxation processes (Flowing Afterglow with Langmuir Probe—FALP).

A lot of FALP apparatuses for recombination study have been already designed (see Table 1). To study the collisional-radiative recombination in cold plasma special low-temperature version of high-pressure flowing afterglow—CRYO-FALP—was developed in our laboratory, which allows us to measure recombination rate coefficient at the temperatures as low as 40 K.

Motivation for apparatus creation is fact, that previous CRR experiments was carried out at high temperatures and it is only several works with electron temperatures below 300 K in our laboratory. Also CRYO-FALP give us opportunity for experimental studies of elementary processes in cold plasmas and also in connection with the formation of antihydrogen (Hu et el. [2005] predict differences for \( T_e < 0.01 \) eV).

CRYO-FALP: construction and processes

The CRYO-FALP is an upgraded version of the standard FALP apparatus. It operates in a wide range of temperatures (40–300 K) and at adjustable pressures (400–2000 Pa) at electron number density \( \approx 10^9 \) cm\(^{-3}\). Because of this large extention of experimental conditions, it can be used to study binary and ternary processes and their temperature dependences.
High purity helium (>99.999%) is used in the experiments as a buffer-carrier gas. Microwave discharge (with power ≈ 10–30 Watts) is ignited in helium, whose pressure can be adjusted in the range about 400–2000 Pa. Obtained plasma contains electrons, He+ ions and excited helium atoms at metastable states (HeM). The metastables are destroyed with the downstream addition of Argon (concentration is [Ar] ≤ 10^{14} cm^{-3}) by Penning ionization and Ar+ dominated plasma is formed.

Chemical processes in the flow tube was developed and numerically solved by [Glosík et al., 2003], [Plašil et al., 2008], [Korolov et al., 2008]. They are following:

\[
\begin{align*}
\text{He}^+ + 2\text{He} & \rightarrow \text{He}_2^+ + \text{He}, \\
\text{He}^+ + \text{He}^M & \rightarrow \text{He}_2^+ + \text{e}, \\
\text{He}^M + \text{Ar} & \rightarrow \text{Ar}^+ + \text{He} + \text{e}, \\
\text{He}_2^+ + \text{Ar} & \rightarrow \text{Ar}^+ + 2\text{He},
\end{align*}
\] (3a–3d)

Concerning the construction of the CRYO-FALP, which has been recently built in our laboratory, it is a stainless-steel tube approximately 5 cm in diameter and over 70 cm long. The reaction zone by itself consists of three parts (Fig.1). The first part (A) serves for the inlet of the reactant gases. For this purpose there are a few ports along the tube, so that the composition of the afterglow plasma can be simply modified and controlled. In our case Ar is added to form Ar+ dominated plasma. This part of the apparatus is kept at the room temperature (300 K). The second part (B) is a precooling part. Its main aim is to facilitate the operation of the coldhead. This zone is cooled by the liquid nitrogen and its temperature is near 100–120 K. The rate coefficient and diffusion measurements by themselves are conducted in the third part (C). This section is connected to the coldhead of a closed cycle refrigerator. The temperature of the coldhead can be set in the range 30–300 K. The flow tube is placed in a large vacuum chamber and connected with the coldhead by copper wires. For better contact thermal paste is used between the coldhead and the wires. Despite this, we still lose some cooling power, so we can not achieve the temperature of the section C less than 40 K. Without the thermal paste usage the temperature of the third zone would be near 50 K and the time of the cooling would increase greatly. We are still working on improving of the insulation and the contact between the tube and the coldhead to get as low temperature as possible. Temperature of the wall is monitored by 6 sensors of different types (silicon diodes, thermocouples type T) mounted along the wall of the flow tube.

In the sections A and B ion-molecule reaction described by (3a–3d) occur to form the Ar+ dominated plasma for decay study. In these parts relaxation processes take place as well. Their time is approximately 50 ms and it depends on the pressure and the flow rate of He. This exceptionally long decay time enables us to measure rate coefficients of even very slow recombination processes, such as collision-radiative recombination.

### Table 1. The most cited versions of the FALP apparatuses.

<table>
<thead>
<tr>
<th>Location</th>
<th>Principal investigator</th>
<th>Special feature</th>
<th>Temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Birmingham, UK</td>
<td>Adams, N.G., Smith, D.</td>
<td>The Selected Ion Flow Tube (SIFT)</td>
<td>300</td>
<td>[Smith and Adams, 1988]</td>
</tr>
<tr>
<td>Georgia, USA</td>
<td>Adams, N.G.</td>
<td>Variable temperature 80–600 K (VT-FALP)</td>
<td>80–600</td>
<td>[Adams, 1992]</td>
</tr>
<tr>
<td>Pittsburg, USA</td>
<td>Johnsen, R.</td>
<td>Optical spectrometer</td>
<td>80–300</td>
<td>[Gougousi, Johnsen and Golde, 1995]</td>
</tr>
<tr>
<td>Fukuoka, Japan</td>
<td>Tsuji, M., Nishimura, Y.</td>
<td>Optical spectrometer</td>
<td>300</td>
<td>[Tsuji et al., 1995]</td>
</tr>
<tr>
<td>Rennes, France</td>
<td>Rowe, B.R., Mitchell, J.B.A.</td>
<td>Movable mass spectrometer (FALP-MS)</td>
<td>300</td>
<td>[Mostefaoaei et al., 1999]</td>
</tr>
<tr>
<td>Prague, Czech republic</td>
<td>Glosik J.</td>
<td>High Pressure Flowing Afterglow (HPFA)</td>
<td>130–300</td>
<td>[Glosik and Plašil, 2000]</td>
</tr>
<tr>
<td>Rennes, France</td>
<td>Novotny O.</td>
<td>Flowing Afterglow With Photoions (FLAPI)</td>
<td>130–300</td>
<td>[Novotny et al., 2005]</td>
</tr>
<tr>
<td>Massachusets, USA</td>
<td>Miller T., Viggiano A.</td>
<td>Quartz tube</td>
<td>300–1200</td>
<td>[Miller et al., 2010]</td>
</tr>
<tr>
<td>Prague, Czech republic</td>
<td>Glosik J., Kotrik T.</td>
<td>CRYO-FALP (without coldhead), high pressure</td>
<td>77–300</td>
<td>[Kotrik et al., 2010]</td>
</tr>
<tr>
<td>Prague, Czech republic</td>
<td>Glosik J., Kotrik T.</td>
<td>CRYO-FALP (with coldhead), high pressure</td>
<td>40–300</td>
<td>[Kotrik et al., 2011]</td>
</tr>
</tbody>
</table>
Figure 1. Scheme of the CRYO-FALP apparatus. Temperature of section A is 300 K and of the section B is near 100–120 K. The temperature of the section C can be adjusted in the range 40–300 K.

For the recombination rate coefficient measurement we need to know the plasma decay in time. It can be found from the time of flight correlation:

$$t \sim \frac{Z}{V_{\text{flow}}},$$  \hspace{1cm} (4)

where $t$ is decay time, $V_{\text{flow}}$ – flow velocity in the tube and $Z$ – distance of the decay.

An axially movable Langmuir probe is used to measure electron density and monitor plasma decay. It moves from the beginning of the section C to the end of the flow tube ($Z_{\text{max}}=35$ cm). The reliability of the Langmuir probe for electron density measurements is well established (see e.g. [Korolov et al., 2008], [Chudacek at el., 1995] and [Swift et al., 1970]).

**Determination of electron temperature by monitoring diffusion losses**

Now in our laboratory we are exploring the following CRR process:

$$\text{Ar}^+ + e^- + e^- \rightarrow \text{Ar} + e^-.$$  \hspace{1cm} (5)

For this reaction formula (2) is used for the recombination rate coefficient calculation. For the temperature range and electron densities, which we operate in, the first term contributes more than 90% of total recombination. It means that the other two terms can be neglected. Thus, we can assume that the rate coefficient depends only on the electron temperature:

$$K_{\text{CRR}} = \alpha_{\text{CRR}} / n_e \cong 3.8 \times 10^{-5} T_e^{-4.5} \text{ cm}^6 \text{s}^{-1}. $$  \hspace{1cm} (6)

The balance equation for the process (5) in quasineutral plasma ($[\text{Ar}^+] = n_e$) is:

$$\frac{dn_e}{dt} = -K_3 n_e^3 - \frac{n_e}{\tau_D},$$  \hspace{1cm} (7)

where $\tau_D$ is diffusion time constant and $K_3$ is ternary rate coefficient.

Actually, we can not surely say that electron and wall temperatures are equals, that is why while measuring, the electron temperature can be found through diffusion to check this. Ambipolar diffusion is considered as a second mechanism after recombination that removes charged particles in the afterglow. Low-temperature plasma is greatly affected by electron losses due to the electron diffusion towards the walls.

The diffusion enters formula (7) with the diffusion time constant:

$$\tau_D = \frac{\Lambda^2}{D_a},$$  \hspace{1cm} (8)

where $D_a$ is ambipolar diffusion coefficient and $\Lambda$ is fundamental diffusion length.

The diffusion time constant can be calculated from the relation between diffusion and reduced mobility $K_0$ of Ar$^+$ ions in helium. This relation is well known and was given in [Mason and McDaniel, 1988]:

$$\frac{1}{\tau_D} = 4.63 \times 10^{15} \frac{K_0(T)}{\Lambda^2} \frac{T}{[\text{He}]} \text{s}^{-1},$$  \hspace{1cm} (9)

where $K_0$ is reduced mobility, $T$ is gas and electron temperature, $[\text{He}]$ is density of Helium.
Figure 2. Upper panel: Experimental data of [He]/τD\text{Expt} versus T for different helium pressures and flow rates. Asterisk symbols: data measured at 250 and 300 K. Solid line: values of [He]/τD\text{theory} calculated from the mobility of Ar\textsuperscript{+} in He. Dashed lines: values calculated for the temperature deviations ± 10 K. Lower panel: ratio τD\text{Theory}/τD\text{Expt} versus measured temperature T. Dashed lines: deviation from the unity that would result if the actual gas temperature differed by ± 10 K from the measured wall temperature. Data are taken from [Kotrik et al., 2011].

A graph of measured values of [He]/τD has to be the straight line with the correct slope, because of nearly constant mobility for the temperatures below 300 K. If we take into account the slight increase of zero-field mobility in the range from 77 to 300 K, the graph should represent a small deviation from the linearity.

The plot of measured values [He]/τD\text{Expt} vs T and theoretically calculated values of [He]/τD\text{Theory} is shown in Fig. 2. Interpolation at intermediate temperatures and zero-field mobilities were used to calculate τD\text{Theory}. Dashed lines in the upper panel indicate [He]/τD\text{Theory} calculation, assuming that actual gas temperature is higher or lower by ± 10 K than the measured wall temperature. The ratio τD\text{Theory}/τD\text{Expt} is shown in the lower panel of the Fig. 2. As well as before, the alternate dashed lines refer to the temperature deviations of ± 10 K.

Also Fig. 2 shows that the experimental values of [He]/τD almost follow the expected temperature dependence. At lower temperatures the diffusion data are less accurate because the late afterglow decay is still affected by recombination, and there may be small residual difference between the gas and wall temperatures.

Conclusions

Collisional-radiative recombination is important in many discharge and astrophysical plasmas, in cold plasmas. The basics of the collisional-radiative recombination were given. The new upgraded version of the FALP apparatus (CRYO-FALP) allows to make experiments in cold plasma down to 40 K.

Using method of electron temperature determination through ambipolar diffusion losses, we can find that electron temperature almost equals the wall temperature.

Acknowledgments. This work is a part of the research plan MSM 0021620834 financed by the Ministry of Education of the Czech Republic and was partly supported by GACR (202/07/0495, 205/09/1183, 202/09/0642, 202/08/H057), by GAUK 92410, GAUKto 54010, GAUK 353811 and by COST Action CM 0805 (The Chemical Cosmos).

References