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Recombination in deuterium plasma at cryogenic temperatures (down to 130 K)

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Abstract. In the presented study variable temperature Flowing Afterglow with Langmuir Probe – VT-FALP was used to study plasma decay in D₂/He mixture at temperatures down to 130 K and total pressure up to 10 Torr. Large extend of partial number densities of D₂ (10¹²-3x10¹⁵cm⁻³) were used in the experiments. Langmuir probes and mass spectrometers were applied to monitor decay of the plasma during the afterglow. The study is continuation of our previous measurements of recombination rate coefficients of D₃⁺ and D₅⁺ ions. In these studies we observed dependence of the recombination rate coefficient on partial pressure of deuterium indicating that third-body assisted recombination is efficient and significantly contributes to recombination in decaying deuterium-containing plasma.

In He/D₂ mixture at low D₂ number densities ions D₃⁺ dominate the ion composition in the afterglow, the plasma decay is controlled by recombination of D₃⁺ ions (with rate coefficient α_3). At high D₂ number densities and lower temperatures ions D₅⁺ are effectively formed and plasma decay is controlled by recombination of D₅⁺ ions (α_5). In the intermediate region the decay of plasma is governed by recombination of both ions with electrons and by ion molecule reactions (forward three-body association and reverse collision induced dissociation), which are keeping equilibrium between D₃⁺ and D₅⁺: $D_3^+ + D_2 + He \leftrightarrow D_5^+ + He$. In the equilibrium ratio $[D_5^+]/[D_3^+] = K_C[D_2]$, where K_C is the equilibrium constant. If the mentioned four processes are dominant processes during the afterglow the decay of plasma can be described by an overall (apparent) effective recombination rate coefficient α_{eff} , which can be expressed by equation: $\alpha_{eff} = (\alpha_3 + \alpha_5 K_C[D_2]) / (1 + K_C[D_2])$. The temperature dependence of observed recombination rate α_{eff} is coupled with the temperature dependencies of α_3 and α_5 and predominantly with strong temperature dependence of K_C given by van't Hoff equation. From the measurements at low partial number densities $[D_2]$ ($=10^{12}$ - 3×10^{13} cm⁻³) where influence of formation of D₅⁺ can be neglected dependence $\alpha_3 = \alpha_3(T)$ was obtained. From the data at intermediate and higher $[D_2]$ values K_C and α_5 were estimated and are reported in the paper. Obtained results are in good agreement with thermodynamic data.

Introduction

The ions H₃⁺ and D₃⁺ play important roles in the kinetics of media of astrophysical interest (interstellar molecular clouds [Geballe et al., 2000; Millar et al., 2000] and planetary atmospheres [Miller et al., 2000]) and also in laboratory produced plasmas (discharges, fusion plasmas at walls [Janev et al., 2000] etc.). The recent discovery of H₃⁺ in diffuse interstellar molecular clouds has confirmed the presence of H₃⁺ in space and has opened a problem of the observed high column density, which critically depends upon the recombination rate for H₃⁺ with electrons at low energies [Geballe et al., 2000; Black et al., 2000]. The problem gets more complicated by taking into account the H₃⁺ deuteration process [Millar et al., 2000]. It is also of interest to examine the recombination of isotopic partners D₃⁺ ions in order to obtain a clearer understanding of this complex phenomenon.

The kinetics of the formation of H₃⁺ (D₃⁺) ions in hydrogen (deuterium) containing plasmas is well understood [Plasil et al., 2002]. Equally important for hydrogen and deuterium containing plasmas is to understand the processes of destruction of these ions in collisions with electrons. However, despite enormous efforts, the results of experimental studies determining the rate of recombination of H₃⁺ and D₃⁺ ions with electrons have been found to yield values that vary by at least one order of magnitude from 1×10^{-8} to 3×10^{-7} cm³s⁻¹ for H₃⁺ [Larsson et al., 2000; Jensen et al., 2002; Smith and Spanel, 1993; Canosa et al., 1992] and 2×10^{-8} to 2×10^{-7} cm³s⁻¹ for D₃⁺ [Laube et al., 1998; Gougousi et al., 1995; Smith and Spanel, 1993; Larsson et al., 1997]. Moreover H₃⁺ and D₃⁺ as the simplest triatomic ions, are important examples for testing new quantum-theoretical calculations, but the agreement between theory, experiment and astronomical observations over a large range of energies has not yet been confirmed [Orel et al., 2000; Bates et al., 1993; McCall et al., 2003; Kokoouline and Greene, 2003].

In order to solve the "enigma of H₃⁺" a new afterglow experiment has recently been developed - *Advanced Integrated Stationary Afterglow – AISA* [Kudrna et al., 2000; Glosik et al., 2001; Glosik et al., 2000], which has been used for studying the decay of a pulsed microwave plasma in He/Ar/H₂ and He/Ar/D₂ mixtures. We have

observed a strong dependence of the recombination rate coefficient for D_3^+ ions on the partial pressure of D_2 [Poterya *et al.*, 2002]. In a follow-on study, we extended the range of deuterium number densities up to $3 \times 10^{15} \text{ cm}^{-3}$ and He (buffer gas) pressures up to 10 Torr using a rebuilt UHV apparatus, the *Flowing Afterglow Langmuir Probe – Variable temperature (VT-FALP)*, and so it was possible to examine the eventual role of D_5^+ ions formation at high deuterium number densities. Analogous measurement was previously done with H_2 gas, studying the ions H_3^+ and H_5^+ [Glosik *et al.*, 2003]. The experiments were carried out at several temperatures to enhance the formation of these ions and to describe the temperature dependency.

Experiment

The *Flowing Afterglow Langmuir Probe (FALP)* technique is based on the so-called chemical reactor principle: The buffer gas flowing along the flow tube carries the plasma created upstream in the plasma source. The plasma concentration decays along the tube through diffusion and recombination losses. For electron or ion concentration measurements, a *Langmuir Probe* [Swift *et al.*, 1970] is used that is movable along the axis of the apparatus. Considering the constant velocity of the flowing gas (or plasma respectively) one can convert the position of the probe to the duration of the studied reaction. We have built a high-pressure version of this apparatus – *VT-FALP*. The output nozzle at the end of the flow tube allows the working pressure to be increased up to 20 Torr so that the diffusion losses decrease. For ion identification and ion formation studies, we use a Quadrupole Mass Spectrometer placed statically behind the flow tube. The large difference between the working pressure of the QMS and the pressure in the flow tube requires a differentially pumped chamber with additional ion optics. The *Langmuir probe* (tungsten wire 18 μm in diameter and 7 mm long) is used to determine the electron number densities along the flow tube. It is not possible to use the probe for direct ion concentration measurements – the Langmuir theory for ions is not perfectly valid for our experimental conditions (high pressures). Finally the validation and calibration of the theory used for electron density calculations was done: the well-understood recombination reaction of O_2^+ with electrons was measured and the value of the rate coefficient obtained was compared with values gained using different experimental methods. The ion density is obtained by considering the plasma quasi-neutrality and the dominance of the studied ion (discussed in the ion formation paragraph below) as being equal to the electron density.

For studying H_3^+/D_3^+ ions we have to be able to measure reactions with rate coefficients down to $10^{-7} \text{ cm}^3 \text{ s}^{-1}$. This limit requires minimizing non-recombination losses in comparison to recombination losses. The diffusion losses are fixed by the geometry of the flow tube (at fixed flow rate of buffer gas) so we can only minimize losses due ion-molecule reactions with impurities. The whole apparatus was pumped for a couple of days before the experiment and most important parts were baked. Injected gases were cleaned using zeolite pumps.

The first version of *VT-FALP* has been successfully used for H_3^+/H_5^+ recombination rate coefficient measurements [Glosik *et al.*, 2003]. Recently we have rebuilt the vacuum core of the apparatus with the following main improvements: the flow tube diameter was increased from 17 mm to 50 mm (to decrease diffusion losses) and was double-shielded using one layer filled with cooled ethanol (with liquid nitrogen streaming through copper tubes in the ethanol) and the second with an insulating material and so better temperature stability was obtained.

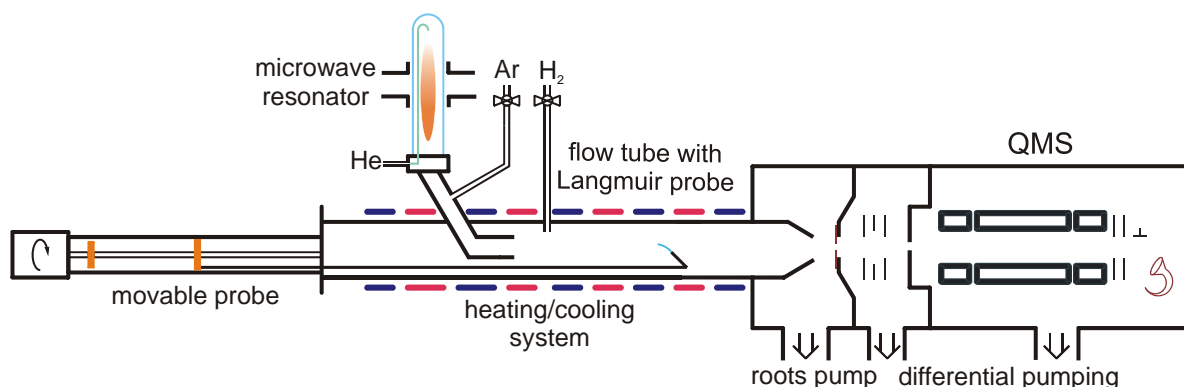


Figure 1. The schematic view of the new *Flowing Afterglow Langmuir Probe – Variable temperature (VT-FALP)* apparatus body. Total displayed length is approximately 1.5 m.

Ion formation

In the D_3^+ experiment, we used the following gas set-up: Pure helium is ionized in a microwave discharge. In addition to He^+ ions it contains also He_2^+ and He^* . In order to remove long-lived helium metastables (He^*), argon is added downstream and an Ar^+/e^- plasma is created. Further downstream, hydrogen is added and D_3^+ ions are created in a sequence of ion-molecule reactions. The kinetics of this process are well understood and the rate coefficients are known. Calculations show that for our experimental conditions ($T < 300$ K, $P_{He} = 9$ Torr, $[D_2] > 10^{13}$ cm $^{-3}$, $[e^-]_0 > 10^{10}$ cm $^{-3}$) the D_3^+ formation time is comparable with the time necessary for the mixing of deuterium with the buffer gas. For more details see *Table 1.* and the numerical model of the reaction kinetics in *Figure 2.* Here you can see one of the advantages of the *Flowing Afterglow* technique in comparison with the *Stationary Afterglow* technique. Individual reactants are added separately which allows reactions to be segregated and reactants are not in contact with energetic electrons that are thermalised downstream in collisions with He. The formation process is thus simpler and more transparent.

We expected that higher number densities of D_2 would enhance the formation of D_5^+ and so in the scanned region of the flow tube plasma one would have $D_3^+/D_5^+/e^-$. We assume also that the plasma is fully thermalised and this assumption is confirmed by the probe measurements of the electron temperature in the decaying plasma.

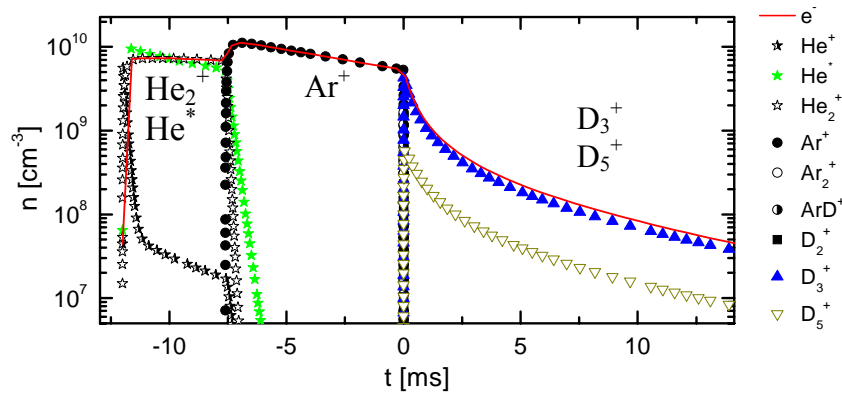


Figure 2. Model of ion-formation process in *VT-FALP*. $T = 300$ K, pressure 9 Torr, flow rate He 6500 sccm $\sim 3 \times 10^{17}$ cm $^{-3}$, flow rate Ar 1.5 sccm $\sim 7 \times 10^{13}$ cm $^{-3}$ (introduced at time -7.5 ms), flow rate D_2 50 sccm $\sim 2 \times 10^{15}$ cm $^{-3}$ (introduced at time 0 ms). Data was obtained by solving the set of partial differential equations corresponding to the set of reactions given in *Table 1.*, including diffusion and recombination losses.

Table 1. Main reactions that take place in the formation of D_3^+ and D_5^+ ions. Reaction rate coefficients are given for 300 K. Typical reaction times were calculated for decay in 9 Torr $\sim 3 \times 10^{17}$ cm $^{-3}$ of He and for $[D_2] = 1 \times 10^{14}$ cm $^{-3}$ and $[Ar] = 7 \times 10^{13}$ cm $^{-3}$. Rate coefficients are taken from the review paper [*Plasil et al., 2002*]. (*) Rate coefficients were deduced from equivalent reactions with hydrogen.

Reaction	Rate coef. [cm 3 s $^{-1}$] or [cm 6 s $^{-1}$]	Reaction time [ms]
$He^+ + 2He \rightarrow He_2^+ + He$	1×10^{-31}	0.1
$He^* + He^* \rightarrow He_2^+ + e$	5×10^{-9}	20
$He^* + Ar \rightarrow Ar^+ + He + e$	7×10^{-11}	0.2
$He_2^+ + Ar \rightarrow Ar^+ + 2He$	2×10^{-10}	0.07
$Ar^+ + D_2 \rightarrow ArD^+ + D$ $\rightarrow D_2^+ + Ar$	7.5×10^{-10} ArD $^+$ production is dominant	0.01
$D_2^+ + Ar \rightarrow ArD^+ + D$	1.5×10^{-9}	<0.01
$D_2^+ + D_2 \rightarrow D_3^+ + D$	1.6×10^{-9}	0.006
$ArD^+ + D_2 \rightarrow D_3^+ + Ar$	4.6×10^{-10}	0.02
$D_3^+ + D_2 + He \rightarrow D_5^+ + He$	$< 1 \times 10^{-29}$ *	>3
$D_3^+ + D_2 + D_2 \rightarrow D_5^+ + D_2$	4.6×10^{-30} , 210 K *	>2000

Data analysis

The detailed description of the measurement and data analysis has been described elsewhere [Glosik *et al.*, 2003; Pysanenko *et al.*, 2002] so only a brief description is given here. Values of electron concentration $n_e(t)$ were obtained using the electron saturated part of the probe characteristics – from the slope of I_e^2 versus probe potential. Due to constant buffer gas velocity in flow tube (18 ms^{-1}) it is simple to convert the position of the probe to reaction time. The electron concentration decay in time is then fitted with a formula including diffusion and recombination losses and the recombination rate coefficient is thus obtained (see example of electron density decays in *Figure 3*). This procedure is possible only in the case of only one dominant ion type or stable equilibrium ratio between ion concentrations in the recombination region.

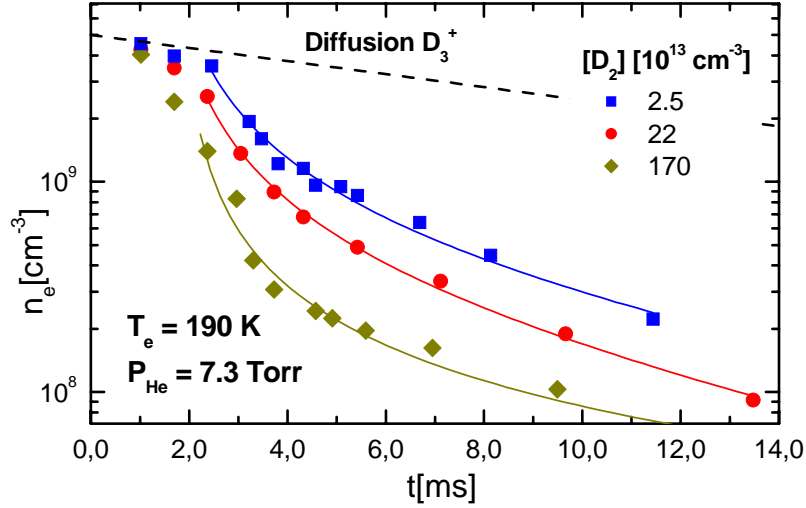


Figure 3. The decay of a plasma containing a mixture of D_3^+ and D_5^+ ions at 190 K and helium pressure 7.3 Torr. The curves were measured at several deuterium number densities. The dashed line indicates expected diffusion losses of D_3^+ in a He buffer gas and solid lines represent fits to the individual data sets.

At low temperatures and high pressures of He and D_2 , formation of cluster ions, D_5^+ , is expected through the reaction



where k_3 is the rate coefficient for three-body association and k_{-3} , the rate coefficient for clusters destruction by collision-induced dissociation (CID) in collisions with He atoms. At the same time, ions recombine with electrons



Here α_3 and α_5 are recombination rate coefficients. When considering processes (1) – (3) and diffusion losses the balance equation for electrons is:

$$\frac{dn_e}{dt} = -\alpha_3 n_e [D_3^+] - \alpha_5 n_e [D_5^+] - ([D_3^+] + [D_5^+]) / \tau_D, \quad (3)$$

where τ_D is the characteristic diffusion time. Let us introduce the ratio $R = [D_5^+] / [D_3^+]$ and realize that $n_e = [D_5^+] + [D_3^+]$. Equation (3) can then be rewritten as

$$\frac{dn_e}{dt} = -(\alpha_3 + R\alpha_5) \frac{n_e^2}{1+R} - n_e / \tau_D = \alpha_{eff} n_e^2 - n_e / \tau_D, \quad (4)$$

where we have introduced an effective rate coefficient α_{eff} . Analysing rate coefficients in process (1) (see reactions rate coefficients in *Table 1*. and model in *Figure 2*.) it was concluded, that the ratio R is constant during plasma decay due to recombination. Then for equilibrium we can write

$$R = \frac{[D_3^+]}{[D_5^+]} = \frac{k_3 [D_2]}{k_{-3}} = K_C [D_2], \quad (5)$$

where K_C is the equilibrium constant, given by the entropy and enthalpy change (van't Hoff equation) [Hiraoka *et al.* 1975]. Using K_C the equation effective for the rate coefficient can be rewritten as

$$\alpha_{eff} = (\alpha_3 + \alpha_5 K_C [D_2]) \frac{1}{1 + K_C [D_2]}. \quad (6)$$

Note the limiting cases where for very low $[D_2]$ value $\alpha_{eff} = \alpha_3$, and high $[D_2]$ $\alpha_{eff} = \alpha_5$. For a detailed explanation see [Glosik *et al.*, 2003].

Results and discussion

We have measured the decay of a plasma in a He/Ar/D₂ mixture at several temperatures ranging from 130 K up to 300 K. The deuterium number density was changed systematically from 2×10^{12} to 2×10^{15} cm⁻³. This large variation allowed us to cover plasmas dominated by the recombination of D₃⁺ ions and by the recombination of a mixture of D₃⁺ and D₅⁺. Due to technical limitations it was not possible to measure the recombination of D₅⁺ only ions at very high partial pressures of deuterium. Figure 3 shows an example of several decay curves measured in one set of measurements at T = 190 K. It is obvious, that the decay of the plasma is dependent on the deuterium number density.

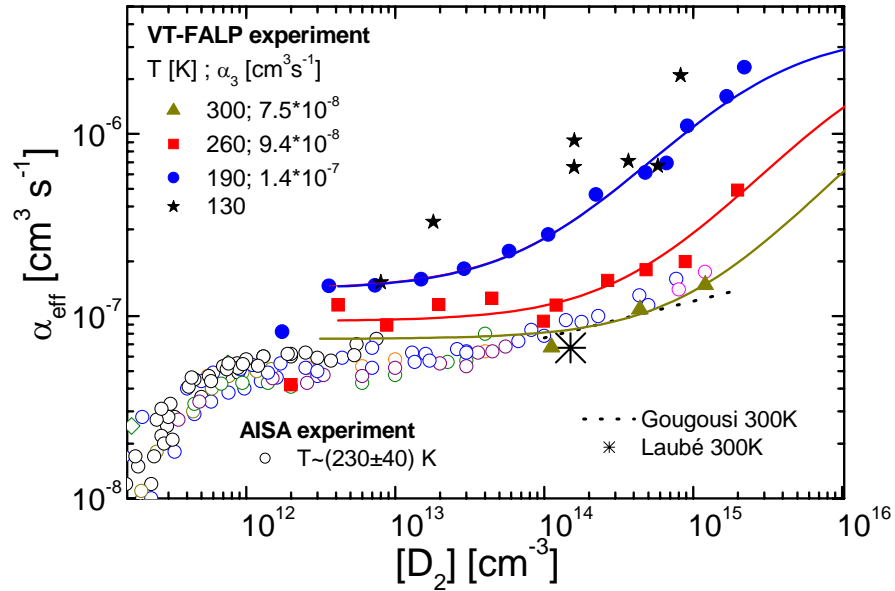


Figure 4. The effective recombination rate coefficients α_{eff} measured over a very broad range of hydrogen number densities on *AISA* (open symbols) and on *VT-FALP* (closed symbols) in a He-Ar-D₂ plasma mixture. The measurements on *AISA* were carried out at the temperature (230 ± 40) K.

The effective recombination rate coefficients obtained at four different temperatures are plotted in Figure 4. Detailed analysis of expected rate coefficients in reaction (1) showed that at the lowest temperature T = 130 K, destruction of D₅⁺ by CID starts to be comparable, or slower than destruction by recombination. In that case equilibrium is not established and formula (6) is not applicable. The following discussion is thus valid only for temperatures 300 K, 260 K and 190 K.

We assume that H₅⁺ and D₅⁺ have similar recombination rate coefficients $\alpha_5 = 3 \times 6 \cdot 10^{-6}$ cm³s⁻¹ and these do not change substantially with temperature (based on our measurement [Glosik *et al.* 2003]). Using this value we can fit the data for specific temperatures with the function (6) to obtain α_3 and K_C . Obtained values of α_3 are written in Figure 4, values of K_C follows here: $K_C(300 \text{ K}) = (1.8 \pm 0.3) \times 10^{-17}$ cm³, $K_C(260 \text{ K}) = (5.8 \pm 0.5) \times 10^{-17}$ cm³, $K_C(190 \text{ K}) = (3.8 \pm 2) \times 10^{-16}$ cm³. The value of $K_C(T)$ thus obtained is in good agreement with thermodynamic data obtained by Hiraoka and Mori, 1989. Values of α_3 at similar temperatures are in good agreement with data from the *AISA* experiment.

The aim of this work was to study influence of the formation of D₅⁺ in a D₃⁺/D₅⁺/e⁻ plasma and to define the regions of partial pressures and temperatures where the formation of D₅⁺ cannot be neglected in the afterglow of a deuterium containing plasma. The study confirms that the pressure dependence of α_{eff} at $[D_2] < 5 \times 10^{13}$ cm⁻³ observed in the *AISA* experiment is not due to the formation of D₅⁺.

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