Recombination of H_2D^+ and HD_2^+ with electrons: a spectroscopic study

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H_2D^+ and HD_2^+ ions, the deuterated isotopologues of H_3^+, play an important role in the chemistry of interstellar medium, especially as precursors for formation of deuterated molecules [1]. The observed column densities can be used as probes of the conditions in different regions of interstellar medium, for example the measured densities of ortho- and para H_2D^+ were used to estimate the age of cloud core forming Sun-like stars [2]. These model calculations strongly depend on the actual values of the recombination rate coefficients of H_3^+, H_2D^+ and HD_2^+.

The recombination of H_3^+ ions with electrons (and to lesser extend also of D_3^+ ions) has been subject of extensive studies for over 50 years (see appropriate chapter in book by Larsson and Orel [3]). There are not so many works on recombination of H_2D^+ and HD_2^+ with electrons [4,5,6,7].

The present experimental study focuses on recombination of H_2D^+ and HD_2^+ ions with electrons, the main aim being the evaluation of possible influence of buffer gas number density on measured recombination rate. The experiments were performed at temperature of 80 K.

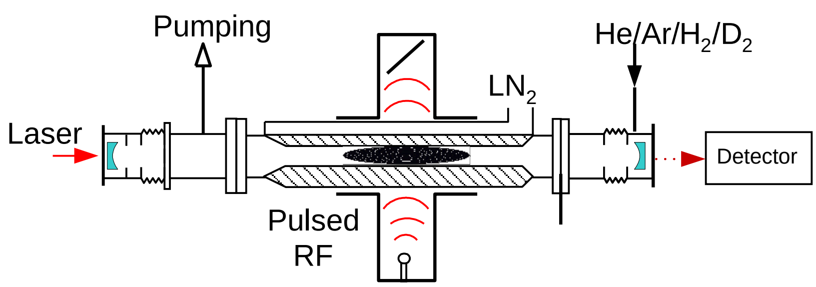

Fig. 1. The SA-CRDS (Stationary Afterglow with Cavity Ring-Down Spectrometer) apparatus. Mixture of $He/Ar/H_2/D_2$ is ionized in a pulsed microwave discharge. The time decays of ion number densities are evaluated from the measured absorbances.

The recombination rate coefficients were measured using stationary afterglow (SA) apparatus in conjunction with cavity ring-down spectrometer (CRDS) to probe the decays of densities of H_3^+, H_2D^+, HD_2^+ and D_3^+ ions. The scheme of the apparatus is shown in Fig. 1. The plasma is generated by a pulsed microwave discharged in a fused silica tube with inner diameter of 1.3 cm. To cut off the power to the magnetron within a fall time of less than 30 μs, the microwave generator is equipped with an external fast high voltage switch. To avoid excessive heating of the gas mixture during the discharge a relatively low microwave power in the range of 5 – 15 W with ~ 40% duty cycle is used. The temperature of the discharge tube can be changed between 80 and 340 K. The discharge itself is ignited in a mixture of He/Ar/H_2/D_2 with typical number densities of $10^{17}/10^{14}/10^{14}/10^{14}$ cm^{-3}. Argon is used for removal of helium metastable atoms and molecules by Penning ionization and to increase the rate of the plasma relaxation after switching off the discharge (for details and discussion see ref. [8]). In a sequence of Penning ionization and ion-molecule reactions the helium ions and metastables, that were created in the discharge, are rapidly converted to a mixture of H_3^+, H_2D^+, HD_2^+ and D_3^+ ions (for further details on the kinetics of formation see [9,10,11].

Table 1. Transitions used in present study. All the listed transitions originate in the ground vibrational state of the corresponding ion. The wavenumbers measured in present study (v_{exp}) are compared to those obtained by Asvany et al. (v_A) [12]. The numbers in parentheses in the fourth column are vibrational quantum numbers of the upper state, (v_1,v_2,v_3) for H_2D^+ and HD_2^+, and (v_1,v_2^l) for H_3^+ and D_3^+. Rotational quantum numbers of the corresponding states are displayed in the fifth column as J_{KaKc} for H_2D^+ and HD_2^+ and J_G for H_3^+ and D_3^+. For details on notation see reference [12].

ion	v_{exp} (cm^{-1})	v_A (cm^{-1})	transition	
H_2D^+	6459.037	6459.036	(0,2,1)	$2_{02} \leftarrow 1_{11}$
H_2D^+	6466.532	6466.532	(0,2,1)	$1_{11} \leftarrow 0_{00}$
H_2D^+	6491.349	6491.349	(0,2,1)	$2_{12} \leftarrow 1_{01}$
HD_2^+	6466.935	6466.936	(1,2,0)	$1_{01} \leftarrow 1_{10}$
HD_2^+	6535.953	6535.953	(1,0,2)	$2_{12} \leftarrow 1_{01}$
HD_2^+	6536.316	6536.319	(1,0,2)	$1_{11} \leftarrow 0_{00}$
H_3^+	6807.288		$(0,3^1)$	$2_3 \leftarrow 3_3$
D_3^+	6848.505		$(0,3^1)$	$3_2 \leftarrow 2_2$

The principal diagnostic technique is the time resolved cavity ring-down absorption spectroscopy in the continuous wave modification (cw-CRDS). The setup is based on the configuration described by Romanini et al. [13]. For further details on the SA-CRDS experimental setup used in our laboratory for the determination of recombination rate coefficients see e.g. [14]. Several DFB (Distributed FeedBack) laser diodes and an ECDL laser (External Cavity Diode Laser) were used to probe the low-laying rotational states of H_3^+, H_2D^+, HD_2^+ and D_3^+. The used transitions are listed in Table 1.

Assuming thermal equilibrium of states, the number densities of H_3^+, H_2D^+, HD_2^+ and D_3^+ can be evaluated from the measured absorbances. If the relative densities of H_3^+

isotopologues are constant during the afterglow, the time decay of electron number density n_e can be described by equation:

$$\frac{\partial n_e}{\partial t} = -\alpha_{\mathrm{eff}\Sigma} n_e^2 - n_e / \tau_{\mathrm{RD}}, \qquad (1)$$

where

$$\alpha_{\mathrm{eff}\Sigma} = \alpha_{\mathrm{effH3}} f_{\mathrm{H3}} + \alpha_{\mathrm{effH2D}} f_{\mathrm{H2D}} + \alpha_{\mathrm{effHD2}} f_{\mathrm{HD2}} + \alpha_{\mathrm{effD3}} f_{\mathrm{D3}} \qquad (2)$$

is the overall effective recombination rate coefficient and τ_{RD} characterizes the diffusion losses. The contributions to the $\alpha_{\mathrm{eff}\Sigma}$ from the different isotopologues of H_3^+ are described by their effective recombination rate coefficients (α_{effH3}, α_{effH2D}, α_{effHD2}, α_{effD3}) and by their fractional population (f_{H3} = $[H_3]/n_e$ etc.). The subscript eff denotes possibility that the recombination rate coefficients of H_2D^+ and HD_2^+ depend on buffer gas pressure due to helium assisted three body recombination as was observed in case of H_3^+ and D_3^+ ions [15]:

$$\alpha_{\mathrm{eff\ ion}} = \alpha_{\mathrm{bin\ ion}} + K_{\mathrm{He\ ion}}[\mathrm{He}], \qquad (3)$$

where $\alpha_{\mathrm{bin\ ion}}$ and $K_{\mathrm{He\ ion}}$ are the binary and ternary recombination rate coefficients, respectively and the subscript "ion" denotes either H_3^+, H_2D^+, HD_2^+ or D_3^+.

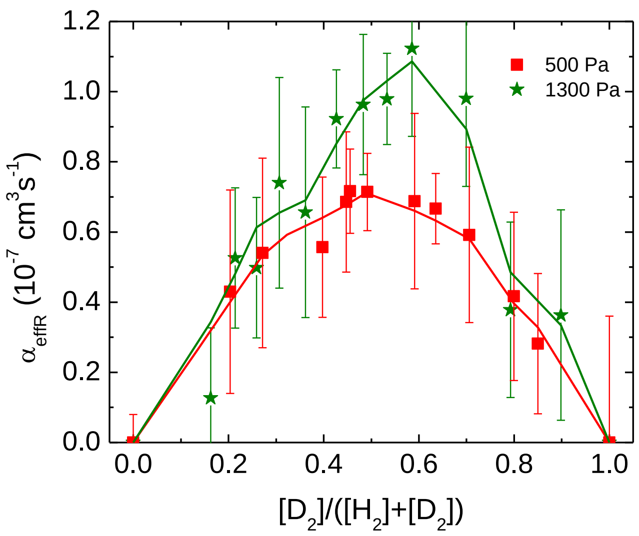

Fig. 2. The dependence of $\alpha_{\mathrm{effR}} = \alpha_{\mathrm{eff}\Sigma} - \alpha_{\mathrm{effH3}} f_{\mathrm{H3}} - \alpha_{\mathrm{effD3}} f_{\mathrm{D3}} = \alpha_{\mathrm{effH2D}} f_{\mathrm{H2D}} + \alpha_{\mathrm{effHD2}} f_{\mathrm{HD2}}$ on $[D_2]/([H_2] + [D_2])$ obtained at 80 K, and 500 and 1300 Pa of helium buffer gas. The increase of the recombination rate with buffer gas pressure is evident. The full line is fit to the data used to obtain α_{effH2D} and α_{effHD2}.

We previously measured the effective recombination rate coefficients of H_3^+ and D_3^+ [16] therefore it is possible to subtract their contributions from $\alpha_{\mathrm{eff}\Sigma}$:

$$\alpha_{\mathrm{effR}} = \alpha_{\mathrm{eff}\Sigma} - \alpha_{\mathrm{effH3}} f_{\mathrm{H3}} - \alpha_{\mathrm{effD3}} f_{\mathrm{D3}} = \alpha_{\mathrm{effH2D}} f_{\mathrm{H2D}} + \alpha_{\mathrm{effHD2}} f_{\mathrm{HD2}}. \qquad (4)$$

The resulting dependence of α_{effR} on $[D_2]/([H_2] + [D_2])$ obtained at 80 K and two different pressures is shown in Fig. 2. As can be seen from Fig. 2, the measured recombination rate α_{effR} increases with increasing pressure (e. g. for $[D_2]/([H_2 + D_2]) = 0.6$, $f_{\mathrm{H2D}} + f_{\mathrm{HD2}} \sim 0.5$, the measured α_{effR} increases from ~ 7×10^{-8} $\mathrm{cm^3s^{-1}}$ at 500 Pa of He to ~ 1.1×10^{-7} $\mathrm{cm^3s^{-1}}$ at 1300 Pa of He). By fitting the $\alpha_{\Sigma\mathrm{eff}}$ using known values of α_{effH3}, α_{effD3} [15] and measured f_{H3}, f_{H2D}, f_{HD2} and f_{D3} we obtained α_{effH2D} and α_{effHD2}. The three body recombination rate coefficients of H_2D^+ and HD_2^+ evaluated from α_{effH2D} and α_{effHD2} using equation (3) are on the order of 10^{-25} $\mathrm{cm^6s^{-1}}$, i.e. similar to those measured at 80 K for H_3^+ and D_3^+ [15]. Further experiments at different temperatures and pressures are in progress.

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