EXPERIMENTAL STUDIES OF DISSOCIATIVE RECOMBINATION OF H_3^+, KrH^+ AND XeH^+.

A.P. Le Padellec, S. Laubé, C. Rebrion,
O. Sidko, J.C. Gomet and B.R. Rowe.

Département de Physique Atomique et Moléculaire, URA 1203 du CNRS,
Université de Rennes I, Campus de Beaulieu,
35042 Rennes Cedex, France.

The exact value of the rate coefficient α for dissociative recombination of H_3^+ ground state ions has been and is still a subject of controversy [(1),(2),(3)]. Following our previous work in helium afterglow, we have measured $\alpha(H_3^+)$, $\alpha(KrH^+)$ and $\alpha(XeH^+)$ in an argon-helium buffer using a FALP-MS apparatus.

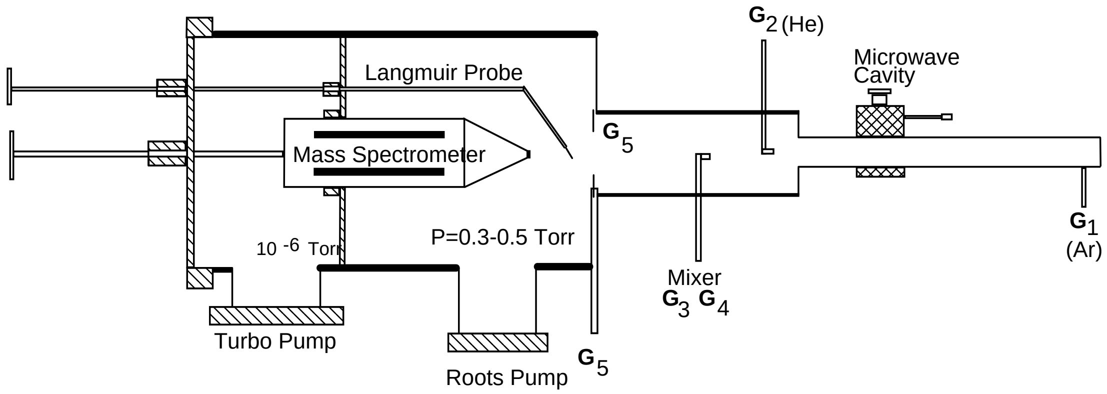

Fig.1:

Figure 1: MS-FALP experimental set-up

Argon flows through the discharge (Gate G_1: Q_{Ar}=30 sl min^{-1} atm) and the electrons are thermalized downstream by large helium injection (G_2: Q_{He}=5 sl min^{-1} atm). It is therefore possible to obtain at low pressure (P~0.5 Torr) a plasma where Ar^+ is the dominant ion. Addition of hydrogen alone results in H_3^+ production through the following reactions:

$$Ar^+ + H_2 \rightarrow ArH^+ + H$$
$$ArH^+ + H_2 \rightarrow H_3^+ + Ar$$

The latter reaction is known to form H_3^+ up to v=2. In this case, $\alpha(H_3^+)$ has been determined to be 1.0 10^{-7} cm^{3}s^{-1}.

When Kr or Xe (Gate G_3) is injected in excess of H_2, (Gate G_4) the plasma is dominated by KrH^+ or XeH^+, these two gazes having proton affinities larger than H_2. The measured values of the rate coefficients for these ions are respectively:

$$\alpha(KrH^+) < 1.0\ 10^{-8}\ \text{cm}^3\ \text{s}^{-1}$$
$$\alpha(XeH^+) = 1.1\ 10^{-7}\ \text{cm}^3\text{s}^{-1}$$

in good agreement with the previous work of Geoghegan [(4)] and coworkers only for KrH^+.

By adding a large quantity of H_2 further downstream (Gate G_5) in a flowing afterglow plasma dominated by KrH^+, it is possible to obtain H_3^+ as a dominant ion through the reaction:

$$KrH^+ + H_2 \rightarrow H_3^+ + Kr$$

with $[H_2] >> [Kr]$ due to the very close proton affinity of Kr and H_2. Since KrH^+ does not recombine, this can be done with a fairly high density. It is therefore possible to measure $\alpha(H_3^+)$ for ions that are almost certainly in their ground state: a computer simulation supports this conclusion.
We have in our disposal two different methods to calculate α (see text below).Depending of the method used, we got :

$$\alpha(H_3^+) = 0.9\ 10^{-7}\ cm^3\ s^{-1} \qquad \text{(Method 1: figure 2)}$$
$$\alpha(H_3^+) = 0.8\ 10^{-7}\ cm^3\ s^{-1} \qquad \text{(Method 2: figure 3)}$$

Considering the uncertainties in the various experiments, this result is in good agreement with the measurements of Larsson and coworkers [(5)]. However it can be taken as showing that the α value for ground state is slightly lower than for excited states.

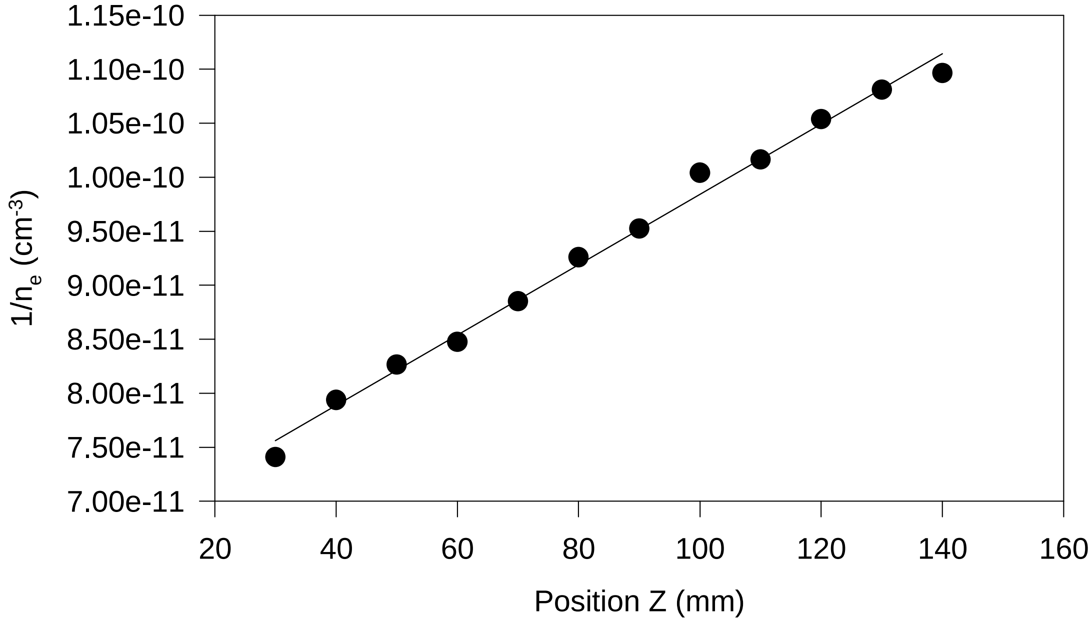

Figure 2: First Method $\alpha(H_3^+)=0.9\times10^{-7}\ cm^3\ s^{-1}$

We dispose of two different methods to deduce the rate coefficient.

1st Method: The slope of the plot $\frac{1}{n_e}$ versus Z yields the ratio α/v. This method does not take into account destruction processes of H_3^+ other than dissociative recombination.

2nd Method: For a fixed position Z relative to a position of reference Z_0, the slope of the plot $\ln\frac{[H_3^+]_Z}{[H_3^+]_{Z_0}}$ versus $\frac{1}{v}\int_{Z_0}^{Z} n_e dz$ yields the rate coefficient. This method takes into account the destruction of H_3^+ by ion-molecule reactions. The only assumption is that the molecule density is constant over the whole range of position Z.

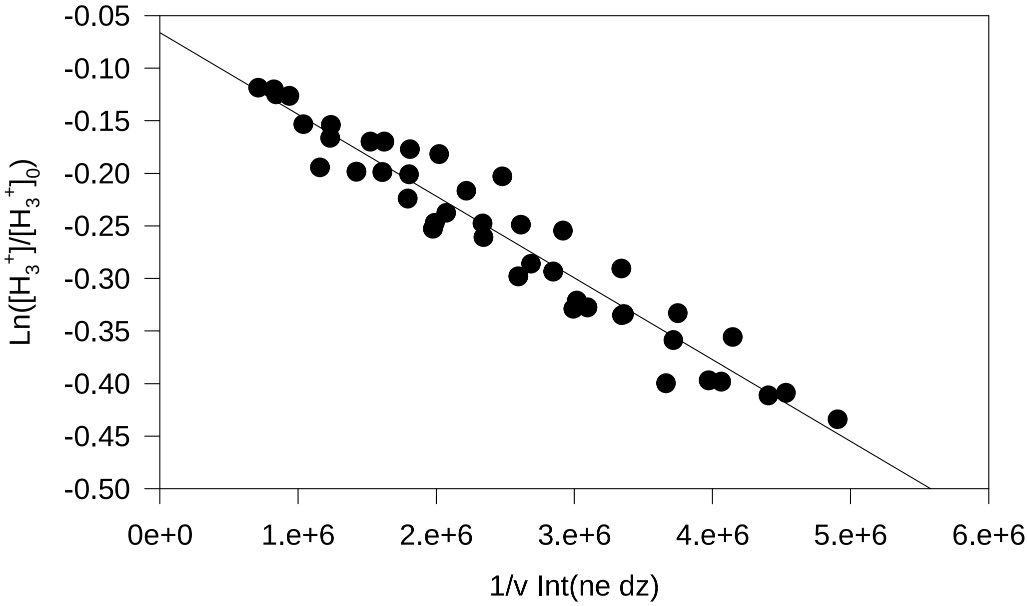

Figure 3: Second Method $\alpha(H_3^+)=0.8x10^{-7}$ cm^3 s^{-1}

(1) A. Canosa, J.C. Gomet, B.R. Rowe, J.B.A. Mitchell and J.L. Queffelec, *J. Chem. Phys.*, **97**, 1028, (1992).
(2) D. Smith and P. Spanel, *Inter. J. Mass Spectrom. Ion Process.*, **129**, 163,(1993).
(3) T. Gougousi, R. Johnsen and M.F. Golde, To be published in *Int. J. Mass. Spectom. Ion Process.*
(4) M. Geoghegan, N.G. Adams and D Smith, *J. Phys. B*, **24**, 2589,(1991).
(5) G. Sundström, J.R. Mowat, H. Danared, S. Datz, L. Broström, A. Filevich, A. Källberg, S. Mannervick, K.G. Rensfelt, P.Sigray, M. Af Ugglas and M. Larsson, *Sci*ence, **263**, 785,(1994).