

# Dissociative Recombination of Acetone Ions with Electrons



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## Introduction

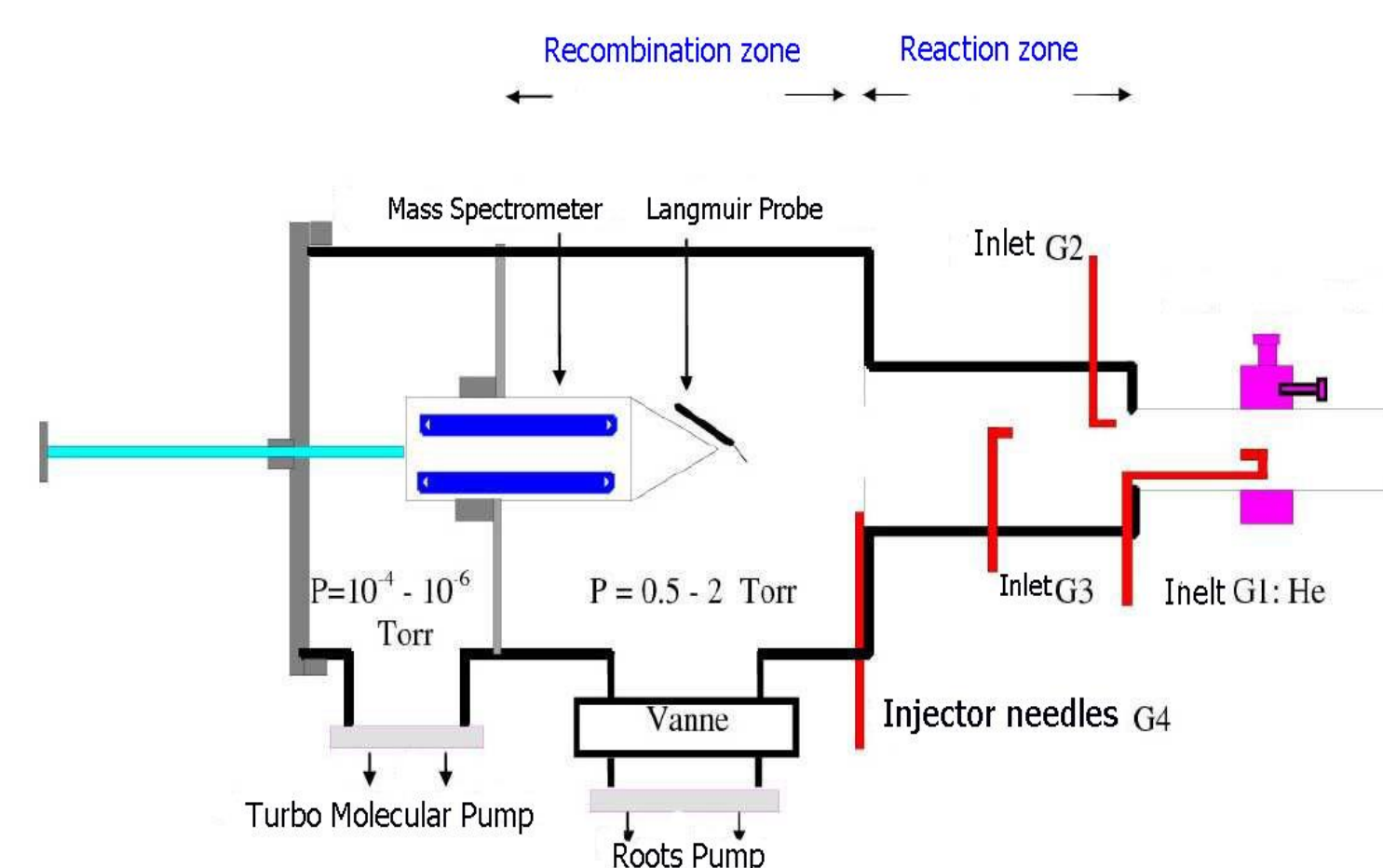
Dissociative recombination (DR) is the reaction in which a molecular ion recombines with an electron and dissociates into neutral fragments, and general reviews of this subject have been given by Florescu-Mitchell and Mitchell [1], Larsson and Orel [2] and Adams and co-workers [3]. This process plays a major role in the evolution and composition of interstellar gas clouds and planetary ionospheres as well as in industrial processing and nuclear fusion plasmas.

The molecule that have been studied is acetone ( $\text{CH}_3\text{COCH}_3$ ). Fragment ions, the parent ion, adduct ions and dimer ions were seen to be formed with relative concentrations which depended upon the density of reagent gas in the flow tube. Dissociative recombination for the individual ions (with the exception of the dimer ions) were then measured using three different measurement protocols. (Values of a few  $\times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$  were found for the ions measured ( $\text{CH}_3\text{CO}^+$ ,  $\text{CH}_3\text{COCH}_3^+$ ,  $\text{CH}_3\cdot\text{CH}_3\text{COCH}_3^+$ ,  $\text{CH}_3\text{CO}\cdot\text{CH}_3\text{COCH}_3^+$ ).

This is an excellent test case for demonstrating the unique character of the FALP-MS apparatus since comparable apparatuses in Europe and the US, which do not have movable mass spectrometers, are generally limited to conditions where only a single ion species is present in the flow.

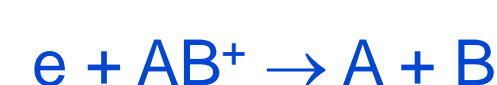
## Experiment Method

A helium plasma is first formed upstream in the flow tube by means of a microwave discharge and then argon gas is titrated into the apparatus to convert helium ions, so formed, into Argon ions. The molecule to be studied is then introduced further downstream in the form of a diluted gas mixture, and charge transfer with the argon ions leads to a chemical ionisation process, to form ions which then react with electrons, created by the microwave discharge.



Sketch of FALP-MS apparatus at University of Rennes1

By measuring the concentrations of electrons and ions using a Langmuir probe and a movable mass spectrometer, respectively, it is possible to determine reaction rate coefficients for the processes of dissociative recombination (DR):



One can be written here to determine reaction rate coefficient, the equation (eq. 1) for the change in the density of the ions  $[M_i^+]$  under study as a function of time,  $t$ , and therefore of distance,  $z$ , along the flow tube, is:

$$\frac{d[M_i^+]}{dt} = v \frac{d[M_i^+]}{dz} = -\alpha_i [M_i^+][e] - k [M_i^+][X] - \frac{D_A}{\Lambda^2} [M_i^+]$$

Where  $v$  is the flow velocity,  $[e]$  the electron density,  $[X]$  the density of a reagent gas,  $k$  the rate coefficient for the reaction between  $M_i^+$  cations with  $[X]$ ,  $z$  represents the position of the mass spectrometer or the Langmuir probe along the flow and  $\alpha_i$  is the dissociative recombination rate coefficient of  $M_i^+$ .  $D_A$  and  $\Lambda^2$  are the coefficient for ambipolar diffusion and the characteristic diffusion length respectively.

The temporal evaluation of  $M_i^+$  ions in the reaction chamber depends upon:

1. Dissociative recombination (DR) with electrons.
2. Ion-Molecule reaction with neutral molecules.
3. Ambipolar diffusion.

If the last two terms in equation (1) are small, and if there is **only one ion present in the plasma**, then  $[M_i^+] = [e]$ ,

$$v \frac{d[e]}{dz} = -\alpha [e]^2 \quad (2)$$

One can then integrate equation (16) to give:

$$\left(\frac{1}{[e]}\right)_z = \left(\frac{1}{[e]}\right)_{z_0} + \frac{\alpha}{v} z \quad (3)$$

and therefore the plot of  $1/[e]$  versus  $z$  is a positive straight line whose slope is  $\alpha/v$ . Multiplication of the slope by the flow velocity  $v$  leads to the recombination rate coefficient  $\alpha$ .

An alternative and more general method for determining the rate coefficient when there is **more than one ion present** is as follows, In the absence of attachment processes, by integrating equation (15) from some initial starting point,  $z_0$  to some position,  $z$ , one obtains the following solution:

$$\ln \frac{[M^+]_z}{[M^+]_{z_0}} = -\frac{\alpha_i}{v} \int_{z_0}^z [e] dz - \frac{1}{v} \left( k [X] + \frac{D_A}{\Lambda^2} \right) (z_0 - z) \quad (4)$$

where  $[M^+]_z$  and  $[M^+]_{z_0}$  are the ion densities at positions  $z$  and  $z_0$  respectively.

By plotting  $\ln [M^+]_z/[M^+]_{z_0}$  versus  $1/v \int_{z_0}^z [e] dz$ , the negative straight line is obtained and the slope of this line giving the recombination rate coefficient  $\alpha$ .

## Results

**At low flow rate** of the acetone mixture of  $5.77 \text{ cm}^3 \text{ min}^{-1}$ , It can be seen that only two terminal ions appear (fig. 1), these being  $\text{CH}_3^+$  and  $\text{CH}_3\text{CO}^+$  formed by reaction 5:

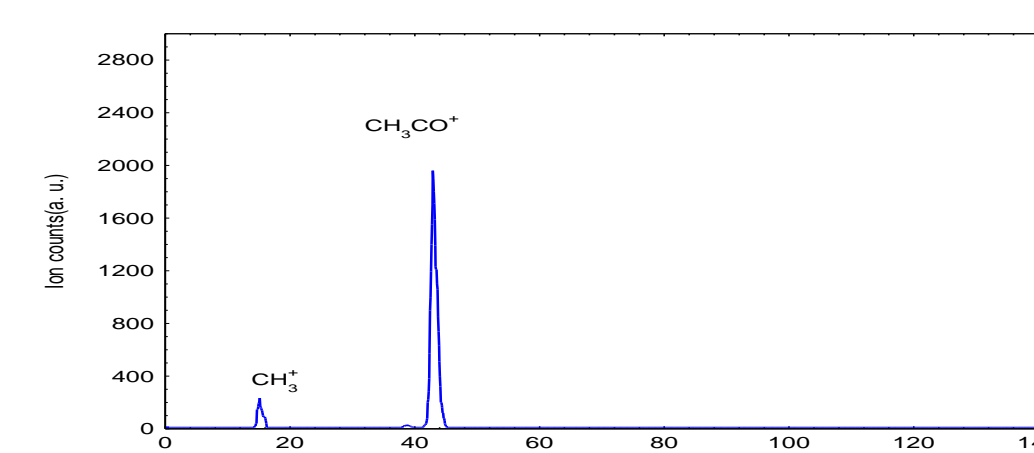
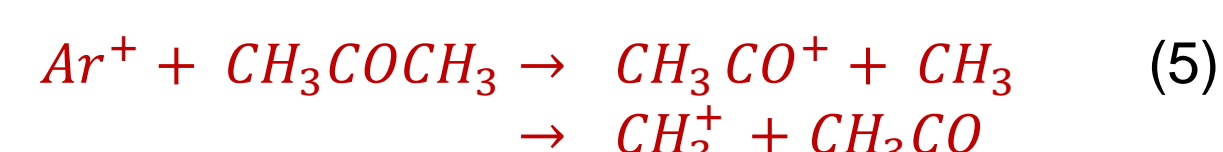


Figure 1

$\text{CH}_3\text{CO}^+$  being highly dominant in the plasma and the rate coefficient could be determined from the slope ( $\alpha/v$ ) of a plot (fig. 2) and the obtained value of DR rate coefficient for  $\text{CH}_3\text{CO}^+$  was  $4.91 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ .

The technique described by equation 4 was also applied to this ion. From this plot, a second determination of the dissociative recombination rate coefficient for this ion, was obtained. This yielded a value of  $4.92 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ , i.e. consistent with the value obtained just by measuring the decrease of the electron density (fig. 3).

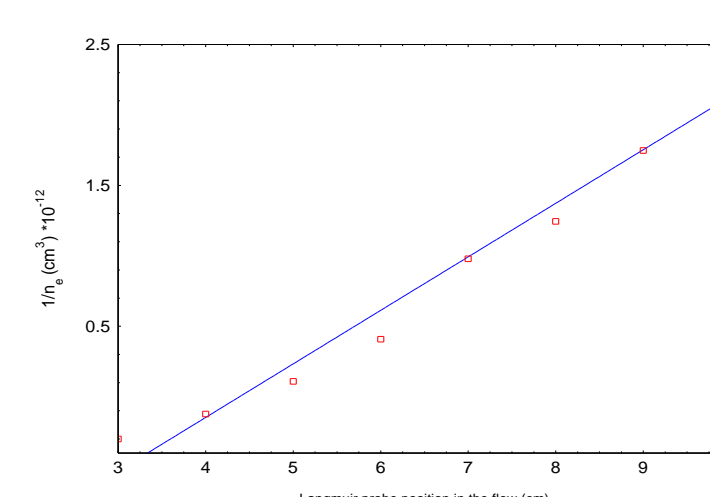


Figure 2

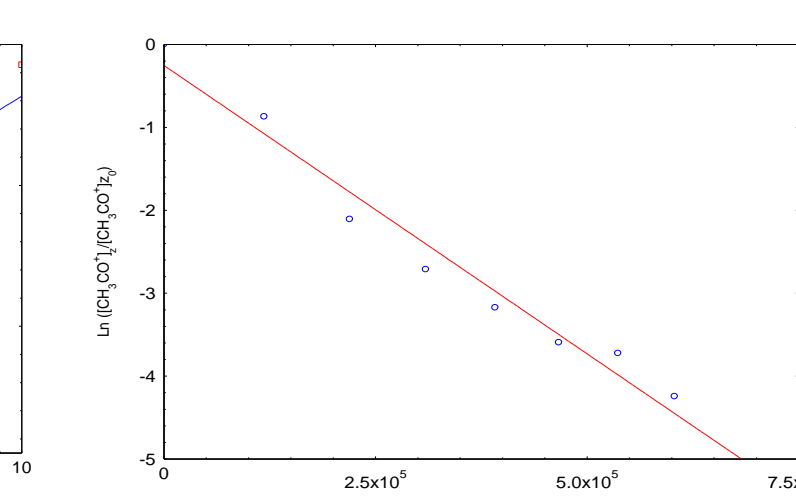


Figure 3

**At a higher flow rate** of  $18 \text{ cm}^3 \text{ min}^{-1}$ , a much more complex spectrum (fig. 4) was found with the acetone ion  $\text{CH}_3\text{COCH}_3^+$ , the adduct ions  $\text{CH}_3\text{COCH}_3\cdot\text{CH}_3^+$  and  $\text{CH}_3\text{COCH}_3\text{CH}_3^+$  and the cluster ion  $(\text{CH}_3\text{COCH}_3)_2^+$ .

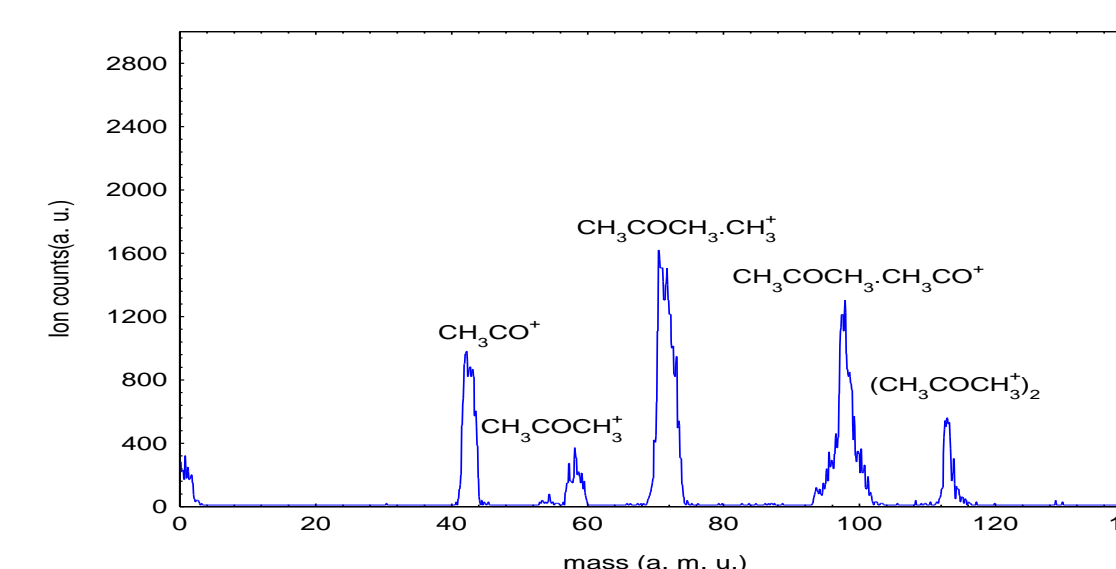
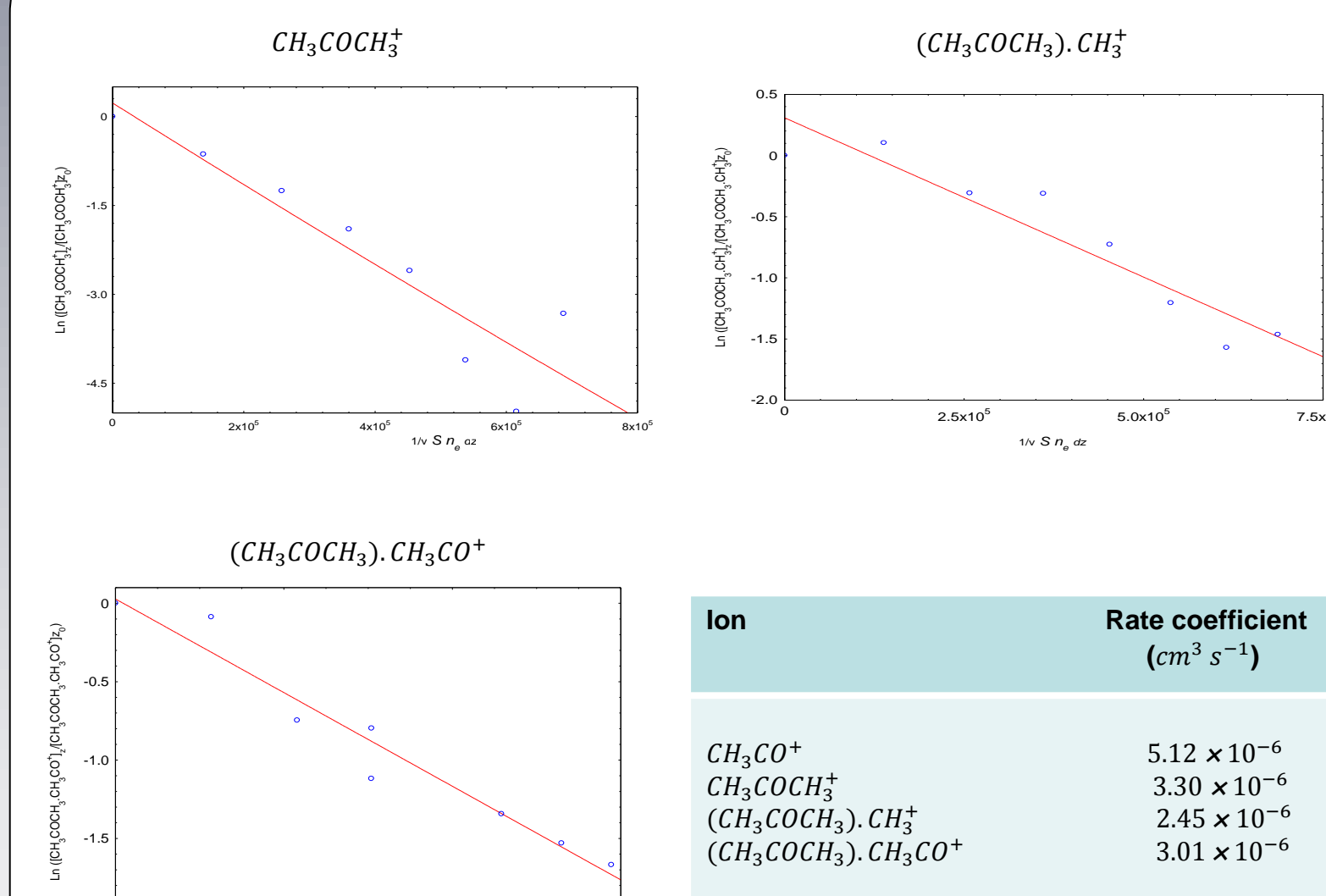


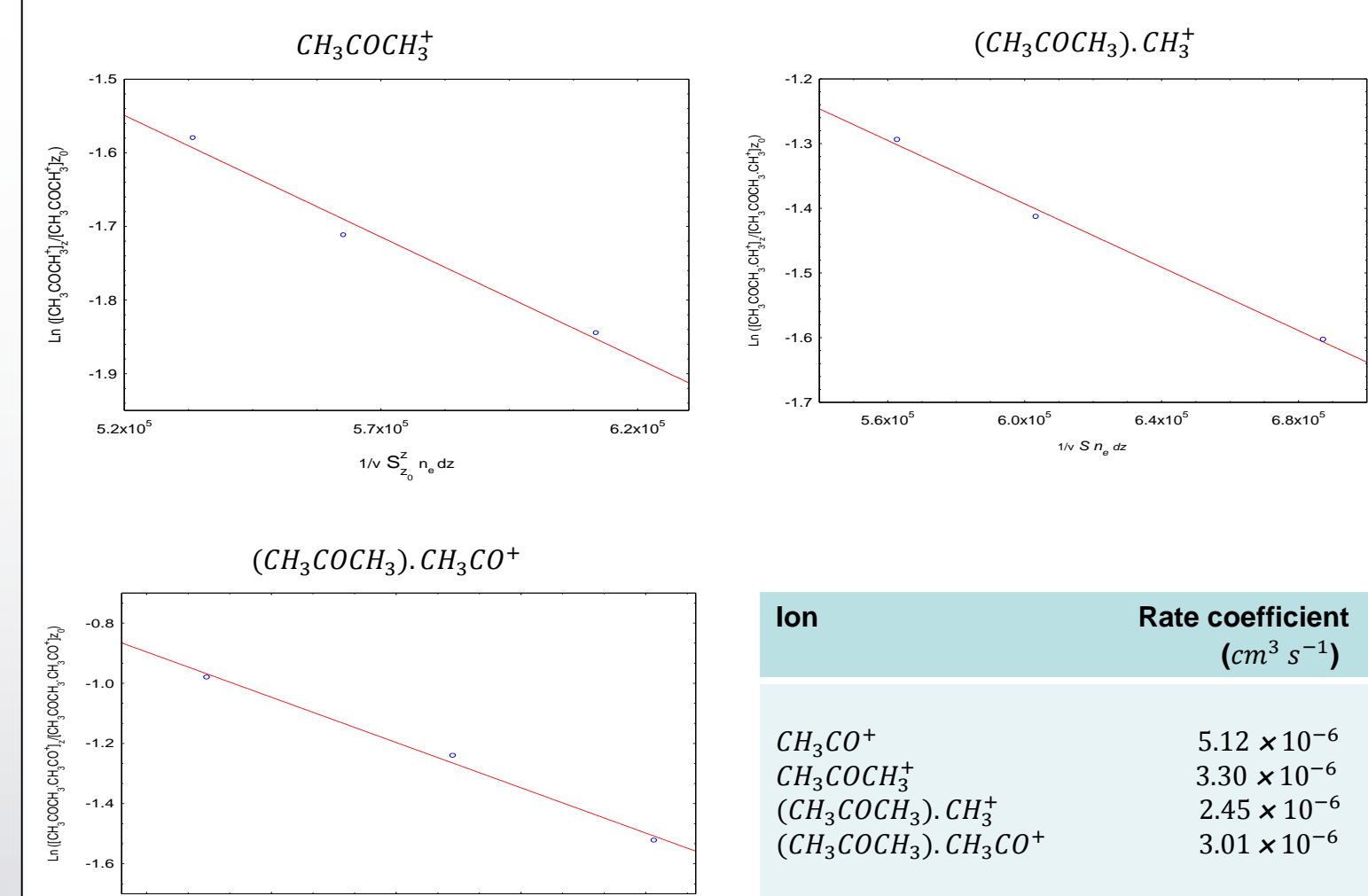
Figure 4

The technique described by equation 4 was used and the rate coefficients so obtained for the dissociative recombination of these ions are listed in Table below.



In the case of the ion-molecule reactions and/or diffusion losses taking place, an alternative method exists. This involves measuring  $1/v \int_{z_0}^z [e] dz$  at fixed  $z$  position "fixed  $z$  method",

This fixed  $z$  method at 3 different electron densities was used to determine the dissociative recombination for these ions:



## Conclusions

□ The full mass spectrum of acetone fragments ions and clusters are obtained at different flow rates.

□ The experimental results of recombination coefficient rate values for  $\text{CH}_3\text{CO}^+$ , acetone, adduct and dimer ions are obtained by different techniques and the obtained values were in good agreement.

## Bibliography

- [1] A. I. Florescu-Mitchell and J. B. A. Mitchell, Phys. Rep. 430, 277–374 (2006).
- [2] M. Larsson and A. E. Orel, Dissociative Recombination of Molecular Ions (Cambridge University Press, Cambridge, 2008).
- [3] N.G. Adams and D. Smith. Chem. Phys. Letters 144, 11 (1988).