CRESU STUDIES OF ELECTRON ATTACHMENT AND PENNING IONIZATION AT TEMPERATURES DOWN TO 48K.

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Introduction

An essential component of the matter in the universe consists of plasma, either in an extremely hot, dense and highly ionized form, (as in stellar atmospheres) or in a much more tenuous, colder and weakly ionized state as in the interstellar medium, circumstellar envelopes and planetary ionospheres. One of the most pressing problems in modern astrophysics is certainly to understand of the birth of stars and of the possible development of associated planetary systems resulting from the gravitational collapse of a dense interstellar cloud [1]. The incredible developments of radioastronomy since the beginning of the 1970's and more recently, the observations from space based satellites (ISO) have resulted in the accumulation of a very large amount of data concerning the interstellar medium and has provided much evidence, in particular in dense interstellar clouds, for the existence of complex, organic molecules. It would be of course extremely significant to be able to understand the chemical evolution of these molecules, that are also observed in the atmospheres of the solar system planets (and of certain of their satellites), from their point of formation from the primitive solar nebula until the present day.

Theoretical astrochemical models, capable of reproducing the evolution of the observed species, are becoming more and more sophisticated, and nowadays include homogeneous phase reactions involving electrons, ions and neutrals, as well as reactions involving neutral species on the surface of grains [2]. Despite this sophistication, we are still very far from a full understanding of this topic and a large numbers of uncertainties exist, particularly with regard to specific reaction rates. The existence of Polycyclic Aromatic Hydrocarbon (PAH) species in a significant density has been proposed to explain several spectral observations, in particular in the infra-red [3]. Given that it is still an object of controversy, the presence of PAH's is now largely accepted. In particular, it has been suggested that certain PAH's can attach electrons. If the negative charges, necessary for the neutrality of the medium, are carried, not by electrons but instead by PAH anions, then all the chemical models will be turned upside down.

These species however, for the most part have very low vapor pressures and the study of their reactions in the gas phase, and in particular at the very low temperatures of the interstellar medium (10-100K) , presents a veritable challenge for the experimenter. The problem of the low vapor pressures encountered at temperatures of the order of 10K, is not limited to the case of the PAH's and in all cryogenically cooled experimental apparatuses, many of the molecules will tend to condense onto the walls, making it impossible to study all species in the gas phase. This is the reason why, at the beginning of the 1980's, Rowe and coworkers [4] established the CRESU method (Cinetique de Reaction en Ecoulement Supersonique Uniforme) in order to study ion-molecule reactions at temperatures down to 8K. More recently, the technique has been applied to the case of neutral-neutral reactions (down to 13K) by using the method of Pulsed Laser Photolysis-Laser Induced Fluorescence (PLP-LIF). The results obtained down to temperatures of 13K have had a profound impact on the models of interstellar chemistry. The object of the present report is to present results obtained for Electron Attachment and Penning Ionization, obtained

with the addition of a Langmuir probe to the measurement apparatus. While the molecules studied are not necessarily of direct interest to the interstellar medium, they have allowed us to validate the technique which can now be extended very easily to the measurement of similar reactions with PAH's.

Experimental

The CRESU technique has been described in detail in a number of articles [4], [5], and in this report we shall limit ourselves to describing only the new aspects that concern the measurement of Electron Attachment and Penning Ionization. Essentially, these include the addition of the Langmuir probe and a mass spectrometer. Since the Langmuir probe has a diameter, less than or equal to the mean free path , which in turn is much smaller than the Debye sheath around the probe, one can expect that any perturbation of the supersonic character of the flow, connected with this measurement, will be very small.

Measurement of the rate coefficients for electron attachment and Penning Ionization are performed using the standard techniques for the flow reactors. For example, in the case of electron attachment, the respective decreases of the electron density, observed at two points along the axis of the flow, downstream from the beam of electrons, are measured as a function of the flow rate of the attaching gas. (Figure 1). Hence one can deduce the value of β. Since the density of the attaching gas is always much greater than that of the electrons, one works in a pseudo first-order condition and therefore, only a relative measurement of the electron density is necessary.

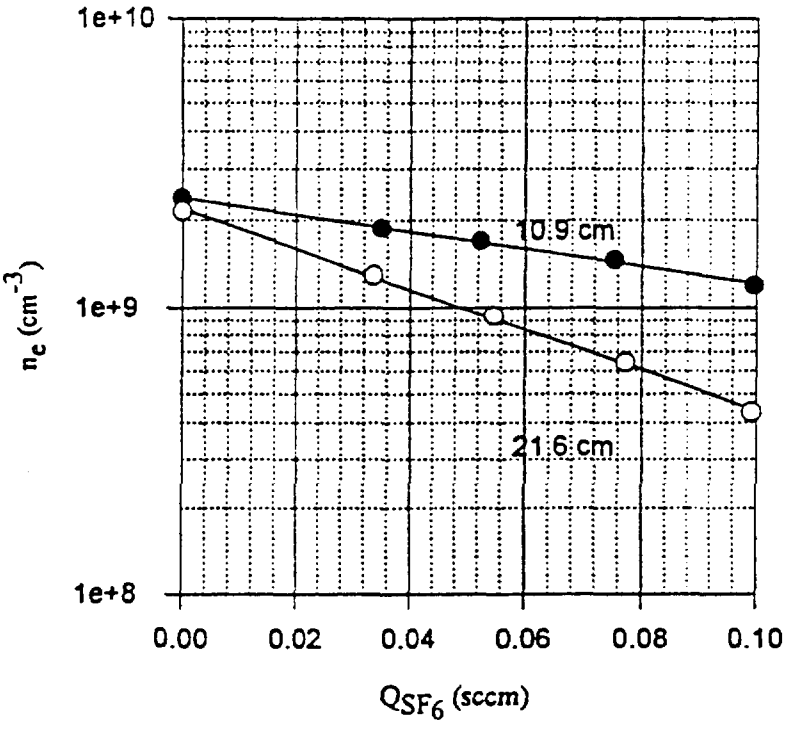

Figure 1 : Electron density as a function of the flow rate of SF_6 at 75 K

Results

The results obtained concerning the attachment of electrons to SF_6 (non-dissociative) and CCl_2F_2 (producing Cl^-) are presented in figure 2. In Table 1, the results for the Penning Ionization of Ar, N_2 and O_2 by metastable helium, are presented.

Molecule	49 K	123 K	157 K
Ar	$4.4\ 10^{-11}$	$3.7\ 10^{-11}$	$3.4\ 10^{-11}$
N_2		$4.1\ 10^{-11}$	$4.2\ 10^{-11}$
O_2			$2.0\ 10^{-10}$

Table 1 : Rate coefficients for the Penning Ionisation of Ar, N_2 and O_2 by Helium metastable

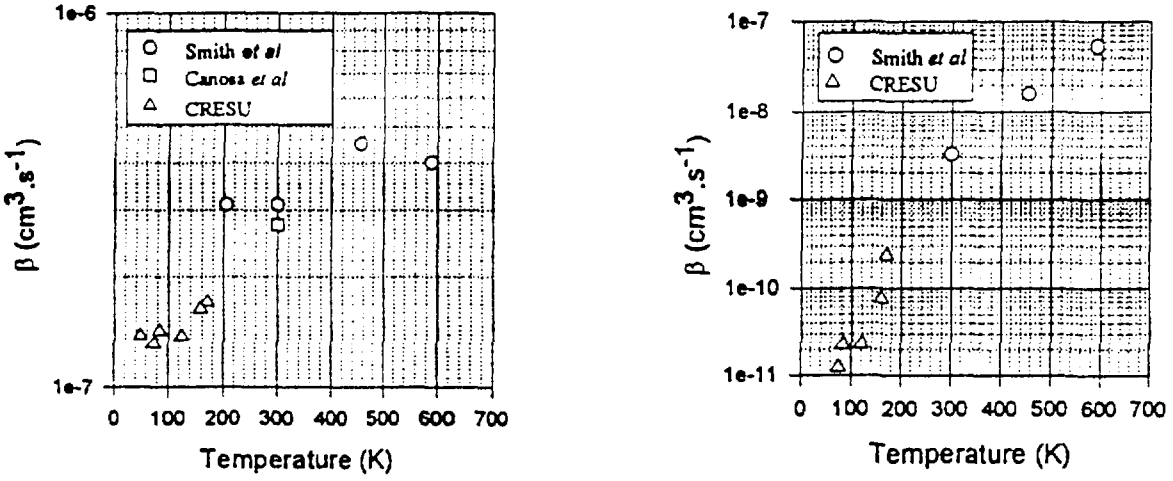

Figure 2 : Rate coefficients for electron attachment of SF_6 as a function ot temperature (at the left) and rate coefficients for electron attachment of CCl_2F_2 (at the right).

In figure 3, our results for the reaction:

$$e + CF_3Br \rightarrow CF_3 + Br^-$$

are compared with those of Smith and Alge [6], [7] Kalamarides et al. [8], and Alajajian et al. [9]. We find very good agreement with the FALP experiment of Smith and Spanel [10]. The differences found between our results and those taken using the other techniques, results from the fact that temperature of the CF_3Br, is held constant at 300K in those measurements while the molecules and electrons in the FALP and CRESU measurements are really in thermodynamic equilibrium. The differences observed, and the variation of the value of β below 100K, provides evidence of the strong influence of the internal state (probably vibrational) of the CF_3Br molecule on its dissociative attachment.

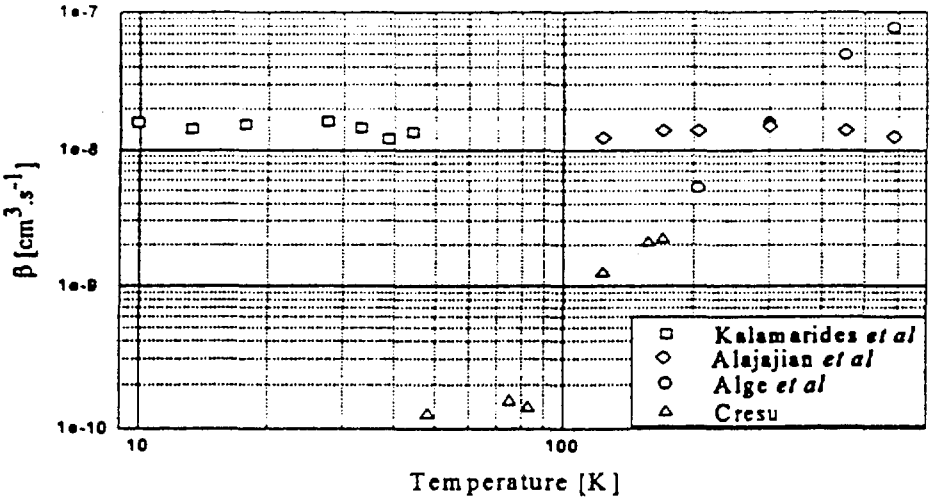

Figure 3 : Comparison with results obtained by Rydberg atom technic, TPE and Falp apparatus

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