Measurement of the recombination of photoproduced PAH ions

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Abstract. A new technique, Flowing Afterglow with Photo Ions – FLAPI, has been developed for measuring the rate coefficient for the recombination of complex ions with electrons. The method is based on the FALP-MS apparatus at the Université de Rennes I. A helium plasma is generated by a microwave discharge in a He buffer gas and downstream a small amount of argon gas is injected to get rid of helium metastables. A very small amount of neutral PAH molecules is added to the afterglow plasma by evaporation from a plate coated with the PAH to be studied. PAH ions are then produced by photoionization of the parent molecule using a pulsed UV laser (157 nm). The laser beam is oriented along the flow-tube and so a constant spatial concentration of photoions is obtained. The electron concentration along the flow-tube is measured by means of a movable Langmuir probe. The decay of the ion concentration in time is measured at a fixed position using a quadrupole mass spectrometer which is triggered by the laser pulse. Anthracene ion recombination has been studied using this technique and we have obtained the preliminary recombination rate coefficient (1.1 ± 0.5) × 10⁻⁶ cm³s⁻¹.

1. Introduction
Polycyclic aromatic hydrocarbon (PAH) molecules and ions are present in the interstellar environment. After years of discussion (see e.g. [1]) it is believed that PAHs are responsible for the so-called ‘unidentified infrared’ and ‘diffuse interstellar bands’ [2, 3]. Astrochemical models describing the life-cycle of PAHs chemistry show electron-ion recombination as very important neutralization channel (see e.g. [4]). Unfortunately very few data in this field are currently available and models usually use estimated values of recombination rate coefficients.

The experimental techniques for studying isolated PAHs are still in development. The FALP-MS technique (Flowing Afterglow with Langmuir Probe and movable Mass Spectrometer, see detailed description in [7]) was used for studying reactions such as electron-PAH cation recombination and electron attachment on neutral PAHs ([5,6]), but measurements of recombination rate coefficient run up against technical problems: Typically quite high concentrations (~ mTorr) of neutral PAH are required to convert all precursor ions to PAH ions via charge transfer reactions and thus fulfill the constraint induced by the mathematical treatment of the kinetic equations. In that case electron attachment may be very effective and the measurement of the electron density by the Langmuir Probe may be affected. Moreover, at high neutral densities the pollution of internal apparatus surfaces with re-condensated PAHs is non-negligible. Especially a pollution of the Langmuir Probe (tungsten wire of typical diameter...
25 \mu m) may influence the electron density measurement. Although a new heated probe was developed [8], measurements of recombination rate coefficients continued to be “dirty”. After a few days of experimental work it was necessary to disassemble and clean the whole apparatus, particularly the mass spectrometer. Furthermore, the classical analysis of data fails when electron attachment to the neutral PAH occurs, as is the case with anthracene.

Therefore we were looking for another ionization process which requires lower density of neutral PAHs but produces enough PAH ions to perform the measurement.

2. Experiment

2.1. Setup

The present measurement was carried out on the basis of the FALP-MS apparatus (see figure 1). The principle of electron production is the same as in the standard FALP technique. A helium buffer gas flows through a glass tube (4 cm in diameter) and is ionized by a microwave discharge (\( \sim 80 \text{ Watt, } 2.455 \text{ GHz} \)). The plasma thus produced (concentration \( \sim 10^{10} \text{ cm}^{-3} \)) flows down through the reaction zone towards the Quadrupole Mass Spectrometer (QMS). The flow is pumped down by a Roots blower (4000 m\(^3\)h\(^{-1}\)). The electron density is measured in the reaction zone by a movable heated Langmuir probe [8]. A small amount of argon is injected to remove helium metastable atoms by Penning ionization and protect the quartz entrance-window of the laser from coating. The mean flow velocity, measured by a time of flight method, is typically \( v = 160 \text{ m/s} \).

Electron-electron collisions ensure a very fast relaxation of the electron energy distribution [9] which is therefore Maxwellian, as was also shown by a Langmuir probe measurement performed previously in the FALP experiment. Moreover there exist a variety of calculations (see for example [10]) and experiments which show that the electrons will relax quickly toward room temperature (temperature of the helium buffer gas). At our experimental conditions the relaxation time needed to obtain room temperature within 1% can be estimated as 100 \( \mu \text{s} \), which is much shorter than the duration of the processes studied.

PAH neutrals are introduced into the Helium flow by spontaneous evaporation from the plate coated with PAH placed downstream of the discharge cavity. PAH cation production by charge transfer with Ar\(^+\) or He\(^{+}\) is then negligible compared to the amount of ions produced by photoionization in the laser beam. The laser beam is oriented along the flow-tube, the pulse length is 10 ns and its energy 10 mJ. Therefore the concentration of photo-ions produced by the laser pulse is constant along the flow. The concentration of extra electrons produced by photoionization was estimated to be lower than 10\(^8\) cm\(^{-3}\), which is much lower than the electron density produced by the microwave discharge.

![Figure 1. A new apparatus for measuring the rate coefficient for the recombination of complex ions with electrons.](image-url)
Figure 2. Principle of the measurement. The laser beam creates a column of ion density $[A^+]$ which is constant along the flow-tube at time $t = 0$. For explanation of the data analysis an elementary cell of $[A^+]$ flowing with the buffer gas is used (Lagrange description). Note that the electron density $n_e$ is much higher than $[A^+]$ and so recombination may not affect the $n_e$ decay significantly.

Once produced, the PAH ions decay by recombination with electrons, ambipolar diffusion and subsequent recombination on the walls, and by ion-molecule reactions. Electrons could be removed by ambipolar diffusion and by recombination with ions, but the only ion which is expected to recombine effectively is the PAH cation and recombination of all PAH ions cannot affect significantly the total electron density. Additional experiments show that the electron density decays exponentially along the flow-tube with a constant decay time $\tau_e \sim 4 \text{ ms}$ independent of the presence of a PAH source. Moreover, we do not observe any distortion of the Langmuir probe characteristic and so we can neglect electron attachment to PAH neutrals and possible ion-ion recombination.

The density of PAH ions $[A^+]$ as a function of time is measured at a fixed position at the end of the reaction zone by a QMS equipped with Multi-Channel Plates (MCP) connected to a Multi Channel Scaler card (MCS) in the PC. Both laser and measurement by the MCS are triggered by the same trigger pulse with a frequency of 50 Hz. Many decays of the ion density are accumulated and a pure signal is obtained after subtraction of the data measured without the laser beam in the chamber (for an example see figure 3).

2.2. Data analysis
The variation of the density of PAH ions $[A^+]$ in an elementary cell of initial distance $D$ from the QMS (at initial time $t = 0 = \text{triggering time}$, see scheme in figure 2) flowing downstream with the buffer-gas (Lagrange description) can be written:

$$\frac{d[A^+]}{dt} = -\alpha[A^+]n_e(d) - [A^+]K$$  \hspace{1cm} (1)

The first term on the right side describes recombination losses ($\alpha$ is the recombination rate coefficient and $n_e(d)$ is the electron concentration at distance $d = vt$ from the QMS) and the second term includes zero-mode ambipolar diffusion and ion-molecule reactions ($K = k[B] + D_a/\Lambda^2$, where $k$ is the reaction rate of the ion-molecule reactions, $[B]$ the concentration of neutrals undergoing ion-molecule reactions)
with PAH cations, $D_a$ the coefficient of ambipolar diffusion and $\Lambda$ a characteristic diffusion length). After separation of variables and integration over $t$ from 0 to $T$ ($T = D/v$, the time of flight of the studied cell to the QMS) we obtain:

$$
\ln \left[ \frac{[A^+](T)}{[A^+](0)} \right] = -\alpha \int_0^T n_e(d) \, dt - KT
$$

We are able to measure $n_e(d)$ using the movable Langmuir probe and $[A^+](T)$ using the QMS (data at time $t = T$ after trigger). Equation 2 may be not valid for $T$ close to 0 due to the presence of higher diffusion modes shortly after the laser pulse and laser scattering on the QMS entrance lens. Therefore we analyze the data after a relaxation time $T_1$:

$$
\ln \left[ \frac{[A^+](T_2)}{[A^+](T_1)} \right] = -\alpha \int_{T_1}^{T_2} n_e(d) \, dt - KT_2 - T_1
$$

There are two ways to obtain the rate coefficient $\alpha$ using (3). If the losses by diffusion and ion-molecule reaction are small we can neglect the second term on the right side. The plot of $\ln \left[ \frac{[A^+](T_2)}{[A^+](T_1)} \right]$ vs $\int_{T_1}^{T_2} n_e(d) \, dt$ with variable $T_1$ or $T_2$ is a straight line whose slope is $\alpha$. Another way is to fix time limits $T_1$ and $T_2$ and to measure several decays $[A^+](T)$ and $n_e(d)$ with different initial electron densities (using e.g. different positions of the microwave cavity). The second term is then a constant for all measurements and will not affect the slope. Note that the term on the left side of equation 3 doesn’t require absolute measurements with the QMS.

3. Results

This new technique has been used to measure the recombination rate coefficient of anthracene ions ($C_{14}H_{10}^+$, mass 178) with electrons. The recombination rate coefficient of this ion was never measured before due to the too high electron attachment rate on anthracene neutrals, which makes this measurement impossible with the FALP-MS technique.

![Figure 3](image1.png)

**Figure 3.** Examples of MCS spectra. Each symbol corresponds to a particular initial electron density. $T_1$ and $T_2$ are the time limits used in data analysis. Data at earlier times may be affected by non-zero mode diffusion and light scattering on QMS, data at later times are too noisy for analysis.

![Figure 4](image2.png)

**Figure 4.** The plot of $\ln \left[ \frac{[A^+](T_2)}{[A^+](T_1)} \right]$ vs $\int_{T_1}^{T_2} n_e(d) \, dt$ corresponding to the data in figure 3. Error bars have been calculated mainly from statistical errors of the data in the MCS spectra. The rate coefficient $\alpha$ has been obtained from a $\chi^2$ fit of the linear function.
The ionization energy of anthracene (7.44 eV) is very close to the energy of the excimer laser used in this experiment (157 nm ~ 7.90 eV), and so we do not expect a major influence of excited ions.

The measurement has been done at a typical pressure of 0.8 Torr and room temperature (295 K). The initial electron density has been varied between $5 \times 10^8$ and $10^{10}$ cm$^{-3}$. One MCS spectrum was accumulated over $\sim 2 \times 10^4$ laser pulses. An example of a set of MCS spectra for different initial electron densities and the corresponding plot of $\ln([A^+](T_2)/[A^+](T_1))$ vs $\int_{T_1}^{T_2} n_e(d) \, dt$ is shown in figures 3 and 4. The measurement has been done with and without gas cleaning in cold traps but the difference of the obtained rate coefficients $\alpha$ was lower than the calculated errors. The preliminary value of $\alpha$ obtained from all sets of measurements is $(1.1 \pm 0.5) \times 10^{-6}$ cm$^3$s$^{-1}$. A more precise value will be obtained after calibration of the Langmuir probe on recombination of $O_2^+$ with electrons in a forthcoming experiment.

4. Conclusion
The measured value of the anthracene recombination rate coefficient is consistent with rate coefficients of similar PAH ions already studied (see summary in [6]). This value is similar to the rate coefficient of phenanthrene (a geometric isomer of anthracene) which is $\alpha = (1.7 \pm 0.5) \times 10^{-6}$ cm$^3$s$^{-1}$. This first measurement with the FLAPI technique can therefore be considered successful. The main advantage of this technique, compared to the classical FALP-MS, is that the recombination rate can be measured even if electron attachment occurs, and coating of the apparatus with redeposited neutral PAH is avoided thanks to the low density that is necessary to perform the measurement. Moreover, with a 157 nm excimer laser this technique can be used to study any species having a vertical ionization potential lower than 7.90 eV. As the ionization potential of PAHs roughly decreases with mass, heavy species like pyrene and coronene could be studied in the near future.

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