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# Measurement of the $\text{H}_3^+$ destruction rate due to ambipolar diffusion in an AC positive column discharge

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## Abstract

We have developed a method to observe the destruction rate of  $\text{H}_3^+$  in the positive column, which is limited by ambipolar diffusion. This method is based on the competition between the ambipolar diffusion rate and destruction rate by added impurities. The decrease of a velocity modulated  $\text{H}_3^+$  absorption signal was studied when small amounts of  $\text{CH}_4$ ,  $\text{N}_2$ , and  $\text{CO}$  were added to a pure hydrogen AC positive column discharge. The destruction rate constant of  $\text{H}_3^+$  due to ambipolar diffusion was then obtained using a steady-state model and previously reported ion-neutral reaction rate constants. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Hollow cathode and positive column glow discharges have been used for decades by spectroscopists to create molecular ions in the abundance necessary for direct absorption studies. AC positive columns are particularly important in this work because of the high degree of sensitivity and discrimination possible by the velocity modulation technique [1]. Kinetic models of these systems help predict discharge conditions (i.e. current, total pressure, mixing ratios of starting gases) that should increase the steady-state concentration of a species of interest. These models can also help identify the carrier of an absorption spectrum especially when it is

unassignable, such as the recent case of the infrared (IR) spectrum of  $\text{CH}_5^+$  [2].

Kinetic models are constructed by considering the major formation and destruction mechanisms. The production rate of molecular ions in the glow discharge depends on the charge density and ion-neutral reaction cross-sections. Most ion-neutral reaction rate constants have been measured by various techniques [3], and the charge density can be estimated from the electric current through the plasma. Ions are destroyed by either recombination with electrons or reaction with a neutral molecule. In hollow cathode discharges with a large diameter and low electron temperature the destruction rate is approximated by the dissociative recombination reaction rate in the bulk, which is easily obtained if the recombination rate constant is known. This is not, however, the fastest destruction process in the positive column. In these discharges ions migrate radially by ambipolar diffusion and, once they reach the wall of the cell,

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combine very efficiently with electrons in the wall. As a result of the much higher electron temperature and generally narrow cell diameter, this mechanism is substantially faster than dissociative recombination in the bulk of the positive column.

The ambipolar diffusion velocity can be estimated theoretically using the expression [4]

$$v_{AD} \approx -\frac{kT_e}{e} k^+ \frac{1}{N(r)} \cdot \frac{dN(r)}{dr}. \quad (1)$$

The mobility of the cation,  $k^+$ , can be obtained experimentally. Albritton et al. measured the reduced mobility [5],  $k_0$ , for  $H_3^+$  in  $H_2$  to be  $11.1 \pm 0.6 \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$  which is related to  $k^+$  by the expression

$$k^+ = k_0 \cdot \frac{760}{P_{(\text{Torr})}} \cdot \frac{T}{273}.$$

The radial charge distribution,  $N(r)$ , on the other hand, varies considerably with discharge conditions [6] as does the electron temperature,  $T_e$ . From experience we generally assume an electron temperature of 2–3 eV in our positive column. A rough approximation for the charge distribution is  $N(r) = N_0[1 - (r/r_0)]$  where  $r_0$  is the radius of the plasma tube and  $N_0$  is the ion number density in the center of the tube. We then estimate that the ambipolar diffusion rate constant is on the order of  $10^5$  to  $10^6 \text{ s}^{-1}$  for a 1.2 cm diameter discharge tube. This type of estimate, which has been used earlier, is clearly crude. In view of the complexity of the weakly ionized discharges used in spectroscopy [6] it is unclear whether this simple estimate is correct. We need to confirm this value experimentally.

In this Letter, we present a simple method that directly measures the destruction rate of ions by ambipolar diffusion. In this method, we add a small amount of an impurity to a  $H_2$  discharge and measure the resulting reduction of the  $H_3^+$  signal. The amount of the impurity is adjusted so that the  $H_3^+$  destruction by the impurities and by ambipolar diffusion are competitive. We can then determine the destruction rate by ambipolar diffusion since the destruction rate by the impurities can be estimated reliably from published rate constants. This technique is non-intrusive and allows us to study the effective destruction rate in the steady state under plasma conditions typically used in spectroscopy.

## 2. Steady-state model

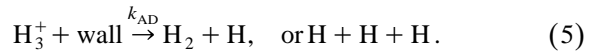
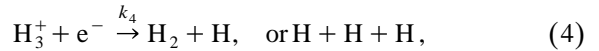
In a pure hydrogen discharge,  $H_3^+$  is created by the two-step process



and



See Table 1 for the values of these and other rate constants.  $H_3^+$  is destroyed by electron recombination either in the bulk (reaction 4) or at the walls of the cell (reaction 5),



$H_2^+$  can also be destroyed by electron recombination, but because the  $H_2$  density is approximately 6 orders of magnitude greater than the electron density and  $k_2 \sim 10^{-2} k_3$ , reaction 3 converts essentially all of the  $H_2^+$  into  $H_3^+$ .

It is worth noting that the dissociative recombination rate constant for  $H_3^+$  has been part of a controversy in recent years [7–10] taking on values from  $10^{-7}$  to  $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . However, even if we assume the highest value of  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$  and the typical electron density of  $\sim 10^{10} \text{ cm}^{-3}$  in the posi-

Table 1  
Reported values of reaction rate constants

$k$	Reaction	Mean <sup>a</sup> ( $\text{cm}^3 \text{ s}^{-1}$ )	Uncertainty <sup>a</sup> ( $\text{cm}^3 \text{ s}^{-1}$ )
$k_2$	$H_2 + e^-$	$(0.4-8) \times 10^{-11} \text{ b}$	–
$k_3$	$H_2 + H_2^+$	$2.04 \times 10^{-9}$	$\pm 0.10 \times 10^{-9}$
$k_4$	$H_3^+ + e^-$	$10^{-7} \text{ c}$	–
$k_6$	$H_3^+ + CH_4$	$2.33 \times 10^{-9}$	$\pm 0.26 \times 10^{-9}$
	$H_3^+ + N_2$	$1.86 \times 10^{-9}$	$\pm 0.24 \times 10^{-9}$
	$H_3^+ + CO$	$2.02 \times 10^{-9}$	$\pm 0.28 \times 10^{-9}$

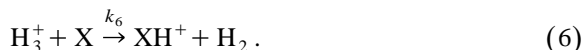
<sup>a</sup> Unless otherwise noted, values are averages of the rates published in Ref. [3] with uncertainties reported at the 95% confidence interval.

<sup>b</sup> Calculated from ionization cross-section published in Ref. [11]. Range is due to uncertainty in the electron temperature of our plasma (assumed to be  $T_e \sim 2-3 \text{ eV}$ ). Since  $k_2$  drops off from Eqs. (10) and (11) this large uncertainty does not affect the results.

<sup>c</sup> See discussion in Section 2.

tive column, the dissociative recombination rate of  $H_3^+$ ,  $10^3 \text{ s}^{-1}$  is still two orders of magnitude slower than the destruction rate of  $H_3^+$  by ambipolar diffusion of  $10^5 \text{ s}^{-1}$ . The ambipolar diffusion is clearly the dominant destruction path for  $H_3^+$  in the positive column of pure hydrogen discharges.

When an impurity species X (where ‘X’ in this work is  $CH_4$ ,  $N_2$ , or  $CO$ ) is introduced to this system, it undergoes ion-neutral reactions:



The  $XH^+$  ions may undergo further reactions, but these have a negligible effect on the steady-state concentration of  $H_3^+$ . Using the rate expressions for reactions 2, 3, 5 and 6, we can write the steady-state condition for  $H_2^+$  and  $H_3^+$ :

$$\frac{d[H_2^+]}{dt} = k_2[H_2][e^-] - k_3[H_2^+][H_2] = 0, \quad (7)$$

and

$$\begin{aligned} \frac{d[H_3^+]}{dt} &= k_3[H_2^+][H_2] - k_{AD}[H_3^+] - k_6[H_3^+][X] \\ &= 0. \end{aligned} \quad (8)$$

We obtain an expression for the steady-state concentration of  $H_3^+$  in a  $H_2/X$  discharge:

$$[H_3^+] = \frac{k_2[H_2][e^-]}{k_{AD} + k_6[X]}. \quad (9)$$

Taking the ratio of expression 9 with and without impurity X and assuming that  $[H_2]$  and  $[e^-]$  do not depend on  $[X]$ , we have

$$\frac{[H_3^+]_{[X]=0}}{[H_3^+]_{[X]}} = 1 + \frac{k_6}{k_{AD}}[X], \quad (10)$$

which depends only on the relative concentration of  $H_3^+$ . For weak absorptions, the intensity of the velocity modulation absorption signal,  $I(H_3^+)$ , is directly proportional to the concentration, so

$$\frac{I(H_3^+)_{[X]=0}}{I(H_3^+)_{[X]}} = 1 + \frac{k_6}{k_{AD}}[X]. \quad (11)$$

This expression shows that  $k_{AD}$  can be determined by simply measuring the relative decrease in absorption signal as a function of the impurity concentration. It is approximated in this formalism that

the addition of the impurity molecules does not affect the ambipolar destruction rate  $k_{AD}$  nor the ion production rate  $k_2[H_2][e^-]$ . We assume this is a good approximation based on the relative independence of plasma current on the impurity concentration, the small impurity concentration of  $[X]/[H_2] < 1/20$ , and the observed variation which approximately matches Eq. (11).

### 3. Experiment

We produced  $H_3^+$  in a liquid nitrogen-cooled, triple jacket positive column of the type used to study  $H_3^+$  and many other ions in the past [13]. Two water-cooled stainless steel electrodes are attached off axis to a 1.2 cm inner diameter pyrex tube of 135 cm length as shown in Fig. 1. The electrodes are situated approximately 3 cm from the bore, so that the main tube sees only the positive column region of the glow discharge. Gas constantly flows into this tube through 18 equally spaced inlets, and is pumped out through 9 equally spaced outlets by a mechanical pump with an approximate flow rate of  $4.5 \text{ m}^3 \text{ h}^{-1}$ . A small port attached to the discharge tube connects to an MKS capacitance manometer. The center bore, inlets, outlets, and pressure gauge port are surrounded by a reservoir of liquid nitrogen. Finally, an outer vacuum jacket insulates the liquid nitrogen reservoir from the atmosphere to prevent condensation of ice. The bellows and spirals along the tube ease stress in the glass due to the large temperature differences between the plasma tube, liquid nitrogen, and ambient air.

IR radiation supplied by a computer-controlled color center laser (Burleigh FCL-20) was multipassed through the AC positive column discharge by the traditional bidirectional White cell [14] configuration and detected by two liquid nitrogen-cooled InSb detectors. Radiation was sent through the cell through two  $CaF_2$  windows mounted at Brewster’s angle. The laser beam was split into two beams of equal intensity and each of the two beams was multipassed unidirectionally in the White cell arrangement through the discharge tube four times in opposite directions for an effective total path length of 10.8 m. Because there were many beams travers-

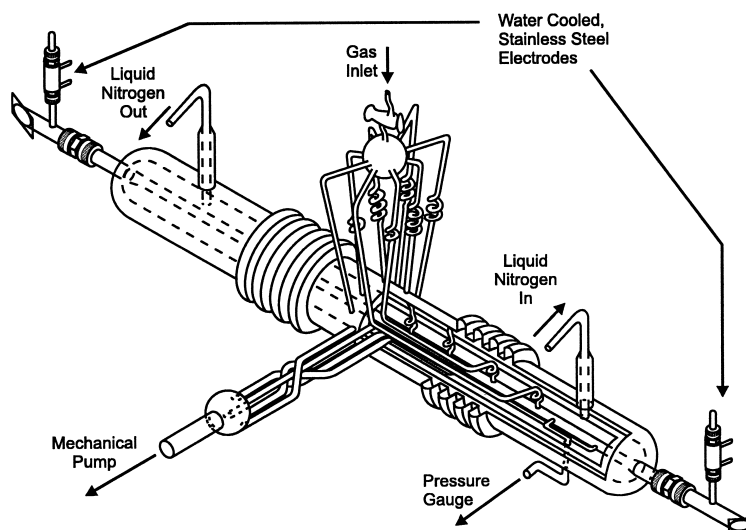


Fig. 1. Liquid nitrogen-cooled positive column discharge cell. The actual cell used in this work had more inlets and outlets but was otherwise identical.

ing the plasma tube in a White cell configuration, the laser probed all radial components of the discharge. Consequently, the measured signal is representative of the average concentration of the absorber<sup>1</sup>. A lock-in amplifier subtracted the two optically balanced signals from the detectors in opposite phase and demodulated the velocity modulated signal at the discharge frequency.

$H_3^+$  was created in a 0.5 Torr hydrogen discharge driven by a  $\sim 6$  kV sine wave at 6 kHz. Ultra-high-purity grade hydrogen (99.999%) was used to ensure that destruction of  $H_3^+$  by impurities in the hydrogen was negligible. We repeatedly scanned the laser across a strong  $H_3^+$  transition [12] ( $\nu_2 \leftarrow 0R(6,6)^-$  at  $3014.358 \text{ cm}^{-1}$ ) with pure  $H_2$  and with small amounts of  $CH_4$ ,  $N_2$ , and  $CO$  added. To study the effects of the destruction rate on ion density and electron temperature, the above measurements were performed at discharge currents (rms) of 150, 175, and 200 mA.

It is necessary to measure the pressure of the impurity gas in the cell accurately. We determined

<sup>1</sup> For this reason, it is clear that we do not measure the genuine ambipolar diffusion. The intent of this experiment is to measure the effective destruction rate constant of  $H_3^+$  due to ambipolar diffusion.

that the correct method for introducing the gases into the cell quantitatively is to first adjust the flow rate of the large concentration gas, in this case  $H_2$ , until the desired pressure is achieved in the cell. Next, a small amount of the impurity gas was allowed to flow into the cell 'on top of' the high pressure gas. We examined the impurity concentration spectroscopically using the strong absorptions of  $CH_4$  which are in the frequency region of the  $H_3^+$  spectral line. We found that if the order of gas introduction was reversed, the impurity gas concentration was overestimated by as much as a factor of 10 for the smallest concentrations (1–2 mTorr impurity versus 0.5 Torr  $H_2$ ).

#### 4. Results and discussion

Fig. 2 shows a plot of the  $H_3^+$  velocity modulated signal as a function of  $N_2$  number density at 200 mA. The observed change in signal intensity follows the dependence expected from Eq. (9) and is emphasized by the dashed function  $a/(b+x)$ . To determine the ambipolar diffusion destruction rate constant, the relative change in  $H_3^+$  signal intensity is plotted versus the impurity number density as suggested by Eq. (11). Two such plots are shown in

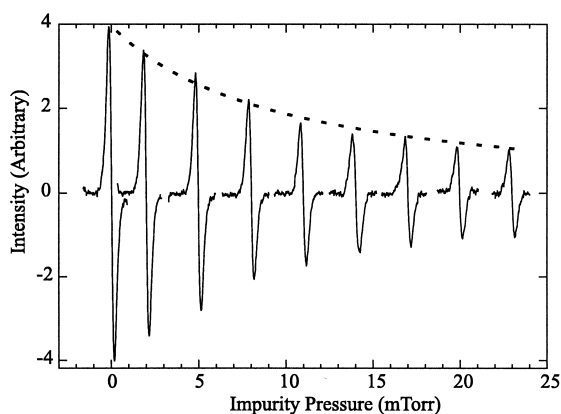


Fig. 2.  $\text{H}_3^+$  signal plotted versus  $\text{N}_2$  pressure at 200 mA. The dashed line is the function  $a/(b+x)$  added to emphasize the agreement with Eq. (9).

Fig. 3. A linear dependence results where the slope is equal to the ratio of the two destruction path rate constants,  $k_6$  and  $k_{\text{AD}}$ . A linear least squares fit was

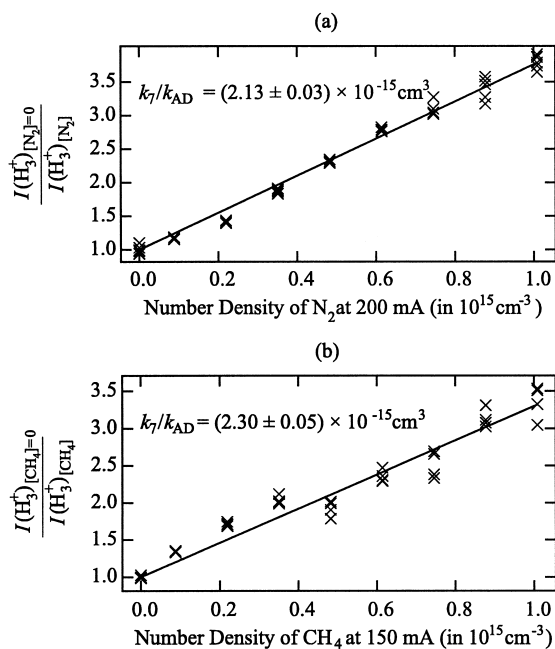


Fig. 3. Two examples of the  $\text{H}_3^+$  relative intensity versus number density of impurity. Each cluster of data contains five measurements. The slope of the least squares fit is equal to  $k_6/k_{\text{AD}}$  as per Eq. (11). Slope uncertainty reported at the 95% confidence interval.

performed by varying only the slope, requiring the y-intercept be equal to 1. The obtained values for  $k_{\text{AD}}$  for all nine trials are tabulated in Table 2.

A consequence of Eq. (11) is that we do not need to determine the absolute concentration of a particular ion, a quantity that is generally difficult to measure accurately. The accuracy of the  $k_{\text{AD}}$  depends only on the accuracy of the measured  $\text{H}_3^+$  intensity ratio, the published values of  $k_6$  and the measured impurity steady-state number density. The accuracy of the signal ratio should be very high because of the large signal-to-noise ratio of the  $\text{H}_3^+$  transition used. Even when the line intensity is decreased by a factor of four for the highest amount of impurity, the absorption signal was still 15 times greater than the noise. Because of this high signal-to-noise ratio and the repeatability in the signal intensity, we estimate that the error in the intensity ratio is on the order of a few percent. The values of  $k_6$  for different impurities have been measured by a variety of techniques. The accuracy of these reported rate constants is approximately 10%. Finally, the method for measuring the pressure of the impurity gas was discussed earlier. The uncertainty in each pressure measurement is  $\sim 1$  mTorr. From these considerations, we estimate the error in this measurement should be no more than 20%.

If we compare the results of different trials, those with the same impurity are consistent in value. There is not a statistically significant dependence of the ambipolar velocity on the discharge current, implying that the electron temperature does not change

Table 2  
Measured destruction rate constants due to ambipolar diffusion

X	Current (mA)	$k_{\text{AD}}$ ( $\times 10^5 \text{ s}^{-1}$ )	Uncert. <sup>a</sup> ( $\times 10^5 \text{ s}^{-1}$ )
$\text{CH}_4$	150	10.1	$\pm 1.38$
$\text{CH}_4$	175	10.0	$\pm 1.38$
$\text{CH}_4$	200	9.96	$\pm 1.38$
$\text{N}_2$	150	5.96	$\pm 0.91$
$\text{N}_2$	175	6.06	$\pm 0.92$
$\text{N}_2$	200	6.74	$\pm 1.02$
CO	150	10.0	$\pm 1.67$
CO	175	9.48	$\pm 1.58$
CO	200	9.48	$\pm 1.60$
Mean		8.66	$\pm 1.83$

<sup>a</sup> Uncertainties reported at 95% confidence interval.

significantly between discharge currents of 150 and 200 mA.

The values of  $k_{AD}$  do, however, depend on the impurity gas used to make the measurement. The values using  $\text{CH}_4$  and  $\text{CO}$  agree within the given uncertainty but those using  $\text{N}_2$  differ by more than the estimated experimental error. The impurity number density accounts for less than 5% of the total gas density in the plasma, and so its presence should not affect the ambipolar diffusion velocity appreciably. A more plausible explanation for this discrepancy is an error in the measurement of the steady-state impurity gas number density. Although the uncertainty in the gas pressure measurement is  $\sim 1$  mTorr, we measure the pressure when the discharge is off and assume that the number density does not change considerably once the discharge is turned on. This assumption *seems* reasonable because the discharge's ionization fraction is only  $\sim 10^{-6}$ . If, however, a substantial number of polymerization reactions occur, the number density for  $\text{CO}$  and  $\text{CH}_4$  would be overestimated, which would artificially increase the estimate of  $k_{AD}$ . On the other hand, for  $\text{N}_2$ , the production of  $\text{NH}_3$  will increase the number of molecules leading to the underestimate of impurities destroying  $\text{H}_3^+$ , and a decrease in the estimate of  $k_{AD}$ . The chemistry of carbon chain growth and  $\text{NH}_3$  production in the plasma is not quantitatively understood, so the extent to which it affects our results cannot be estimated. The actual destruction rate will be between the two values.

To resolve this inconsistency in the measured value of  $k_{AD}$ , this experiment could be repeated with non-carbon containing impurities with high proton affinities (such as  $\text{Xe}$ ,  $\text{Kr}$ ,  $\text{H}_2\text{O}$ , or  $\text{NH}_3$ ) which would not have the chemistry problems discussed above. Each of these species, however, condense in our liquid nitrogen-cooled cell and we are left only with  $\text{CO}$ ,  $\text{N}_2$ , and  $\text{CH}_4$  as the possible impurities.

Regardless of the above mentioned discrepancies, these results provide the first experimental evidence demonstrating that the initial order of magnitude estimate of the  $\text{H}_3^+$  destruction due to ambipolar diffusion in Section 1 is valid for the complicated

weakly ionized positive column discharge. Since the uncertainty in the  $k_{AD}$  presented here is not much worse than the error of most published ion-neutral reaction rate constants, we can now model these plasma chemical systems without having to make any rough order of magnitude estimates. Furthermore, this technique is generally applicable in measuring the effective destruction rates in any type of discharge cell as long as it contains a hydrogen dominated plasma.

## Acknowledgements

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