

Anomalous loss of ionization in argon-hydrogen plasma studied by fast flow glow discharge mass spectrometry

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Changes in ion abundance from the plasma of an abnormal dc glow discharge, using a copper cathode, have been studied as a function of (a) gas residence time in the discharge and (b) the amount of H₂ added to the positive column, without disturbing the discharge. The Ar+H₂ spectra show a severe, but selective, quenching of the ionization. All major ions are quenched except for Cu⁺, which increases in abundance. It is shown that this cannot be explained by either ion-molecule reactions or the fast recombination suggested previously [R. F. G. Meulenbroeks *et al.*, Phys. Rev. E **49**, 4397 (1994)] for such mixtures. The kinetic behavior is consistent with the heavy involvement of stepwise ionization processes in which high excited metastable states of neutral Ar are precursors for most ions observed in the spectrum. It is proposed that these states are rapidly quenched by H₂ down to the Ar(4s) levels, preventing ionization of most species in the discharge, but significantly boosting the Penning ionization of Cu atoms sputtered from the cathode. [S1063-651X(97)10105-2]

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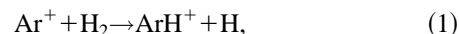
I. INTRODUCTION

The fundamental study of plasmas is important because of their application in thin-film technology, gas lasers, and optical emission and ion sources used for elemental chemical analysis. There is therefore already a vast body of literature devoted to the physical and chemical processes occurring in the different types of discharge and the use of different discharge gases. There has been a continuing interest in the study of mixed plasmas involving Ar/H₂.

In the field of elemental analysis, for example, when H₂ is added to the discharge gas of a conventional glow discharge (GD) mass spectrometer ion source, Saito [1] reported an enhanced sensitivity towards the sputtered metal atom ionization and Smithwick, Lynch, and Franklin [2] reported greater reproducibility in relative sensitivity factors towards the probe species of a multielement cathode. Most recently Tanaka *et al.* [3] reported varying effects on sensitivity towards the ions of nonconducting samples in a rf GD ion source. These authors did not address the fundamental processes involved.

Knewstubb and Tickner [4] (KT) made one of the first detailed studies of the ions from a static discharge by mass spectrometry. They studied both a pure Ar plasma and an Ar/H₂ (1.5%) mixture and discovered "that the addition of H₂ produces a general lowering of the ionization [sic] detected, with a marked lowering of the argon ion concentration." This was attributed mainly to a lowering of the electron temperature and ion-molecule reactions. However, Gordon and Kruger [5], studying an inductively coupled plasma, showed that small amounts of H₂ can have a significant effect on electron densities in the plasma. van de Sanden and co-workers [6,7] recently made Langmuir probe and spectroscopic measurements on a supersonically expanding argon cascaded arc plasma. Again a dramatic reduction in charge density and Ar⁺ was observed with the addition of H₂. In both cases the lost ionization was attributed to the inducement of fast recombination by one route or another.

For example, Meulenbroeks *et al.* [6] proposed that it occurs via the ion-molecule reaction (1) to form ArH⁺. Since ArH⁺ has a recombination coefficient many orders of magnitude larger than Ar⁺ it is presumed to be rapidly removed by reaction (2), this being the vehicle for the reduction of charge:



In this paper we report work carried out using a relatively low pressure, but fast flowing glow discharge ion source, with the hydrogen added either before or immediately after the discharge. The H₂ added downstream did not disturb the discharge and hence did not affect the cathodic sputtering rate. Observations were made by mass spectrometry and this shows directly the dramatic loss of ionization caused. However, the loss is selective. Whereas Ar⁺, ArH⁺ (normally the most abundant ions in the spectrum), and almost all other ions are seen to disappear, Cu⁺ (ionized atoms of copper sputtered from the cathode sample pin) are seen to be significantly enhanced. It is shown from these experiments that neither ion-molecule kinetics nor recombination can explain the behavior.

In optical studies a significant reduction in argon emission (i.e., a quenching of excited states) is also noted when H₂ is added to the discharge [6,5,8,9]. It has also been shown [10,11] that direct ionization may be less predominant in a low-pressure argon positive column than "stepwise" ionization. It is therefore suggested here that most ionization in the region of the discharge sampled by the mass spectrometer occurs by neutral processes involving high excited metastable states of Ar. The kinetic behavior observed for the ions is then consistent with fast quenching, by hydrogen, of the neutral ionic precursors down towards the Ar(4s) levels that populate the Cu⁺ concentration by the Penning reaction.

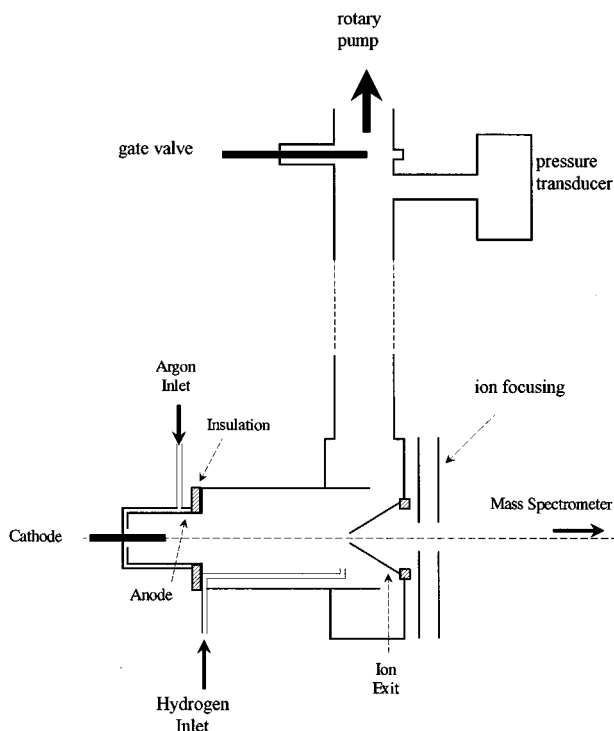


FIG. 1. Schematic diagram of the fast flow glow discharge ion source.

II. EXPERIMENT

The ion source is shown schematically in Fig. 1. A preliminary report has appeared elsewhere [12] and a detailed paper on this technique is in preparation, therefore a brief description only is given here. The cathode in the present study is a Cu pin (2 mm diameter \times 10 mm length) mounted on a probe. The pin is inserted into the hollow anode section (10 mm diameter \times 20 mm length) attached to a short (40 mm length) flow tube (20 mm diameter), also at anode potential. An ion exit cone protrudes into the flow (aperture 0.3 mm). Argon gas passes around the end of the anode, into the discharge, up past the sample pin. The gas is pumped by a $20.5 \text{ m}^3 \text{ h}^{-1}$ rotary pump, via a liquid- N_2 cold trap to prevent backstreaming of rotary pump oil. The source, inside a housing differentially pumped by a 700 l s^{-1} diffusion pump, is mounted on the source bulkhead flange of a double focusing forward geometry mass spectrometer. A secondary gas inlet allows gases to be admitted to the plasma, downstream of the discharge, just in front of the ion exit aperture. Alternatively the gases can be mixed prior to their entry into the discharge tube. The calibrated gas flow rates are measured and controlled using mass flow controllers. A sliding gate valve allows independent control of the pressure in the flow tube. The pressure is measured indirectly at the ion exit aperture by the pressure at the source housing ion gauge. This was calibrated by operating the flow tube under "static" conditions (i.e., with the gate valve closed) and reading the pressure directly using a pressure transducer attached by a short tube to the flow tube, outside the source housing. Temperature is measured by a Pt resistance thermometer inserted into the body of the short flow tube. The knowledge of these three parameters and the geometry allows the flow speed, and hence the gas residence time τ in the plasma afterglow,

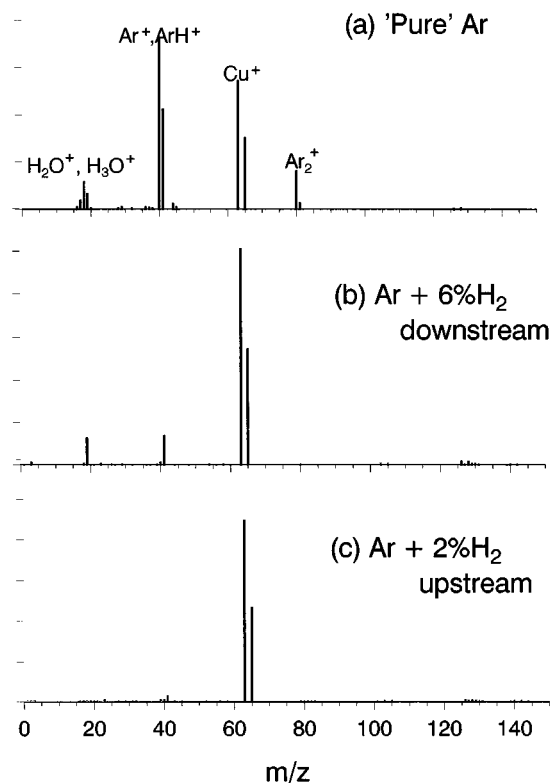


FIG. 2. Examples of GD mass spectra with and without added H_2 : (a) discharge gas: Ar only, $P_2=2$ Torr, $V_1=448 \text{ ml min}^{-1}$, $V_{\text{dis}}=1100 \text{ V}$, $C_{\text{dis}}=4.64 \text{ mA}$; (b) Ar only, $P_2=2$ Torr, $V_1=300 \text{ ml min}^{-1}$, $V_{\text{dis}}=800 \text{ V}$, $C_{\text{dis}}=3.46 \text{ mA}$; but 6% (of V_1) H_2 added at a downstream port; (c) discharge gas: Ar+2% H_2 added upstream, $P_2=2$ Torr, $V_1=300 \text{ ml min}^{-1}$, $V_{\text{dis}}=800 \text{ V}$, $C_{\text{dis}}=4.38 \text{ mA}$.

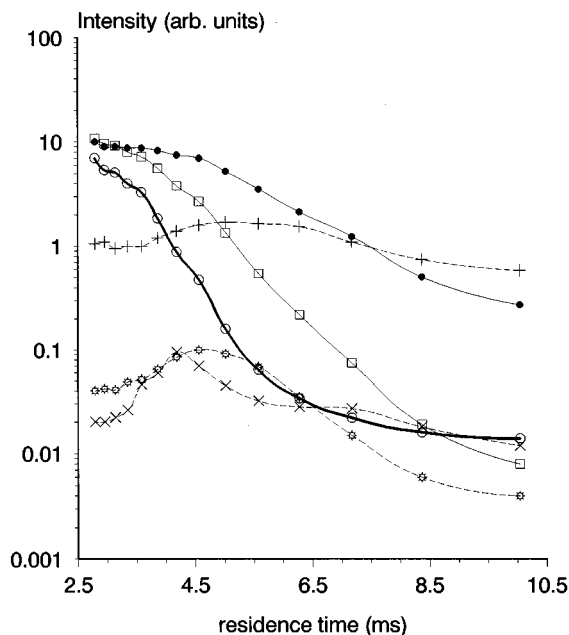
to be calculated and controlled.

A voltage of up to 1500 V at 5 mA could be applied between the anode and cathode and up to -100 V ion extraction (V_{extr}). Gas pressures between 0.5 and 3 Torr were studied and under stabilized conditions the body of the flow tube reached a maximum temperature of approximately 310 K. The cathode surface reaches a temperature on the order of 500 K by sputter heating [13], but the rapid gas flows will ensure that the bulk of the gas down the tube is close to the final temperature of the flow tube walls. The temperature, however, is not critical to the experiments and was constant throughout, to within $\pm 5 \text{ K}$. The mass spectrometer was operated at an accelerating voltage of 4000 eV, the ion beam passing through electrostatic and magnetic (B) sectors before detection using a single channel electron multiplier fitted with an extra collision dynode. The mass spectrum was scanned using B and recorded as peak heights either from the traces on an UV oscillograph or manually from collector meter readings.

The gases used were Ar and He: research grade (BOC, 99.999 97%) and H_2 (BOC, 99.999%). The Cu(99.99+%) was from Goodfellow Metals Ltd.

III. RESULTS

The mass spectra in Fig. 2 show the principle ions produced from the discharge. These are Cu^+ , Ar^+ , ArH^+ ,



Pure Ar, 1 Torr

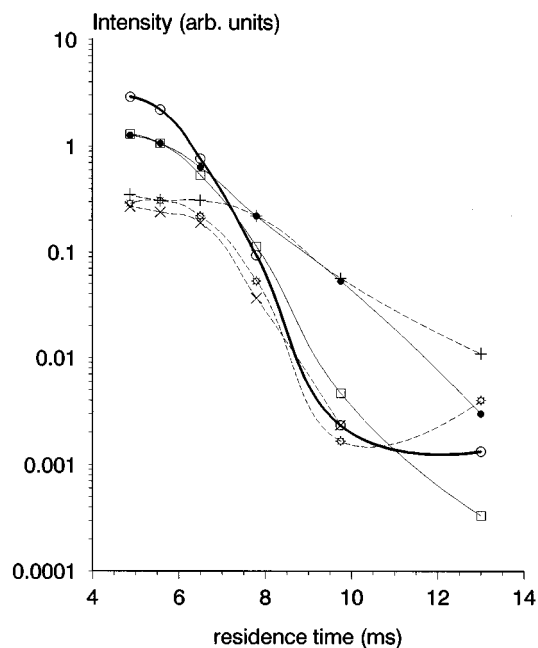
FIG. 3. Relative intensities (logarithmic scale) of ions versus Ar-gas flow (residence) time τ ; $P_2=1$ Torr, $V_{\text{dis}}=550$ V, and $C_{\text{dis}}=2$ mA. \circ , Ar^+ ; \square , ArH^+ ; \bullet , $^{63}\text{Cu}^+$; \times , H_2O^+ ; $+$, H_3O^+ ; \odot , Ar_2^+ .

H_3O^+ , H_2O^+ , and Ar_2^+ . The Cu^+ are of course the ionized sputtered cathode atoms. The water originates from the ppm levels of impurity in the gas and degassing [4,14,15]. The relative ion abundances depend mainly on the pressure and flow rate. Variations are shown plotted as a function of gas flow time in Figs. 3 and 4, at constant pressures of 1 and 2 Torr, respectively. The gas flow time τ is defined as the time required for the gas front to travel distance d (~ 4 cm) from the end of the copper cathode pin to the ion exit aperture. τ is given by Eq. (3), where V_1 is the gas volume flow rate measured at pressure P_1 (1 standard atm) and temperature T_1 (298 K), P_2 and T_2 are pressure and temperature (assumed to be equal to the average wall temperature at 303 K) of the gas in the flow tube, and r is the radius of the flow tube (is equal to 1 cm):

$$\tau = \frac{dP_2T_1\pi r^2}{P_1V_1T_2}. \quad (3)$$

This does not give an accurate value because the pin is recessed inside the narrower ($r=0.5$ cm) hollow anode section of the source and there will be a temperature gradient in the gas as a result of heating up as the gas passes over the cathode. However, no attempt is made here to generate quantitative kinetic data and relative changes in τ will be accurate. The minimum residence time attainable in the present apparatus is at 1 Torr, with $\tau > 2.5$ ms.

Although the ion intensities increase by a factor of 10 when a relatively large ion extraction voltage (greater than -60 V) is applied to the ion exit cone, V_{extr} in these experiments was set at only -5 V with respect to the anode, to



Pure Ar, P = 2 Torr

FIG. 4. Relative intensities (logarithmic scale) of ions versus Ar-gas flow (residence) time τ ; $P_2=2$ Torr, $V_{\text{dis}}=800$ V, and $C_{\text{dis}}=2.1$ mA; only the ^{63}Cu isotope is shown. \circ , Ar^+ ; \square , ArH^+ ; \bullet , $^{63}\text{Cu}^+$; \times , H_2O^+ ; $+$, H_3O^+ ; \odot , Ar_2^+ .

avoid the complication of a significant drift field penetrating into the flow tube. Conditions (pressure P_2 , voltage V_{dis} , and current C_{dis}) in the discharge stayed constant to within $<5\%$ during any particular experiment.

The results of adding H_2 at the downstream port are shown in Figs. 2, 5, and 6. P_2 and τ were kept fixed in each case. The additional gas is catered for by adjustment of the flow rate at the downstream gate valve. For comparison Ar and He were also added (separately) in an identical manner. The main effect with both gases (see Fig. 7) is to cause an increase in the Ar^+ current, a smaller increase in ArH^+ , and a decrease in H_3O^+ , with no significant effect on Cu^+ . However these changes are relatively small, and opposite in direction, by comparison with the addition of H_2 . Note that Fig. 6 is plotted on a logarithmic scale, while Figs. 5 and 7 are plotted normally. It should also be noted that because the secondary gases are added immediately in front of the ion exit their interaction time with the flow gas is much less than τ .

The effects of adding H_2 are dramatic. This is illustrated by comparing the mass spectra for different reaction systems, shown in Fig. 2. Under optimized flow and pressure conditions, in a mixture in which 5% of H_2 is added, the mass spectrum [Fig. 2(b)] shows a nearly pure Cu^+ ion spectrum, with almost complete quenching of all ions except for small contributions from Cu^+ adduct ions: (CuH_2O^+) , (CuAr^+) , and Cu_2^+ (which in the pure Ar flow are hard to detect). The Cu^+ signal is actually significantly boosted, to a degree depending on the conditions involved.

In Fig. 5, $P_2=1$ Torr and $\tau=2.5$ ms, when the initial

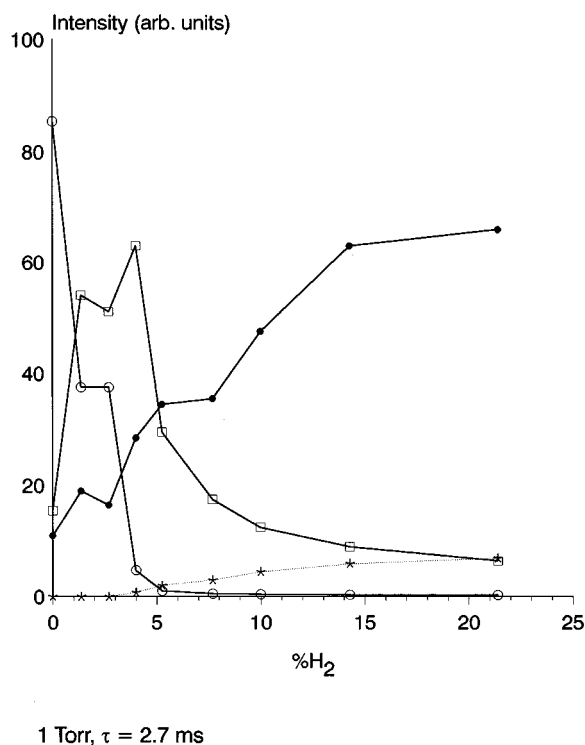


FIG. 5. Relative intensities (normal scale) of ions versus H_2 (percent of the Ar flow rate, $V_1 = 360 \text{ ml min}^{-1}$) added at the downstream port, when $P_2 = 1$ Torr, $\tau = 2.7$ ms, $V_{\text{dis}} = 500$ V, and $C_{\text{dis}} = 2$ mA, \circ , Ar^+ ; \square , ArH^+ ; \bullet , $^{63}\text{Cu}^+$; \star , H_3^+ ($\times 10$).

spectrum gives $\text{Ar}^+ > \text{ArH}^+ > \text{Cu}^+ \gg \text{H}_3\text{O}^+$. As H_2 is added it appears as if Ar^+ is rapidly replaced by ArH^+ in reaction with H_2 . This in turn appears to be replaced by Cu^+ , which increases by a factor greater than 6, as H_2 increases to 15% of the total flow rate. Under the different starting conditions of Fig. 6(a) ($P_2 = 2$ Torr and $\tau = 4.9$ ms) the spectrum (0% H_2) starts with $\text{Cu}^+ \approx \text{ArH}^+ < \text{Ar}^+$. Now, however, Ar^+ and ArH^+ are both rapidly quenched as H_2 is added, ArH^+ at a slower rate. Cu^+ still increases significantly, but much less

so than before. H_3O^+ appears not to be readily quenched. In contrast at much longer residence times [Fig. 6(c), $\tau = 13$ ms] Cu^+ , Ar^+ , ArH^+ , and Ar_2^+ are hardly affected by the addition of H_2 , while H_3O^+ is now rapidly quenched.

The same strong effects were observed when small quantities of H_2 were mixed with the discharge gas upstream of the discharge. This is shown by the spectrum in Fig. 2(c). This system is not so easy to control, however, because mixing the discharge gas changes the discharge conditions.

IV. DISCUSSION

A. Ion-molecule and neutral reactions in the glow discharge

The glow discharge is an intense source of ions, electrons, and excited neutral species [16]. While all are presumed to be present in the short flow tube, only the cations are monitored in the present setup.

It is clear from the spectra that, even though research grade Ar was used, the trace water content is a significant contributor to the chemistry, as is found in static glow discharge devices [4,14,15,17]. The significant gases present in the discharge or the afterglow are therefore mainly Ar, sputtered Cu, H_2O (trace), and, when added, H_2 . The possible (exothermic) ion-molecule and electron-ion recombination reactions involving all these species are listed in Table I, together with their known thermal rate coefficients k where available. Pseudo-first-order rate constants k' are calculated by multiplying k by the number density of the neutral reactant. The rate constants for the charge and proton transfer reactions between Cu, Ar^+ , and ArH^+ , respectively, are not known. However, most simple exothermic ion-molecule reactions occur at close to the Langevin collision frequency [18], except perhaps when they approach thermoneutrality [19] (hence $k_9 \ll k_{9,L}$) and it is this rate that has been used in the absence of experimental data. Charge transfer reactions require "near resonance" to be efficient. It has been suggested [20] that reaction 1 is efficient because there are excited states of Cu^+ close in energy to ground state Ar^+ . The pseudo-first-order rate constants for this reaction have there-

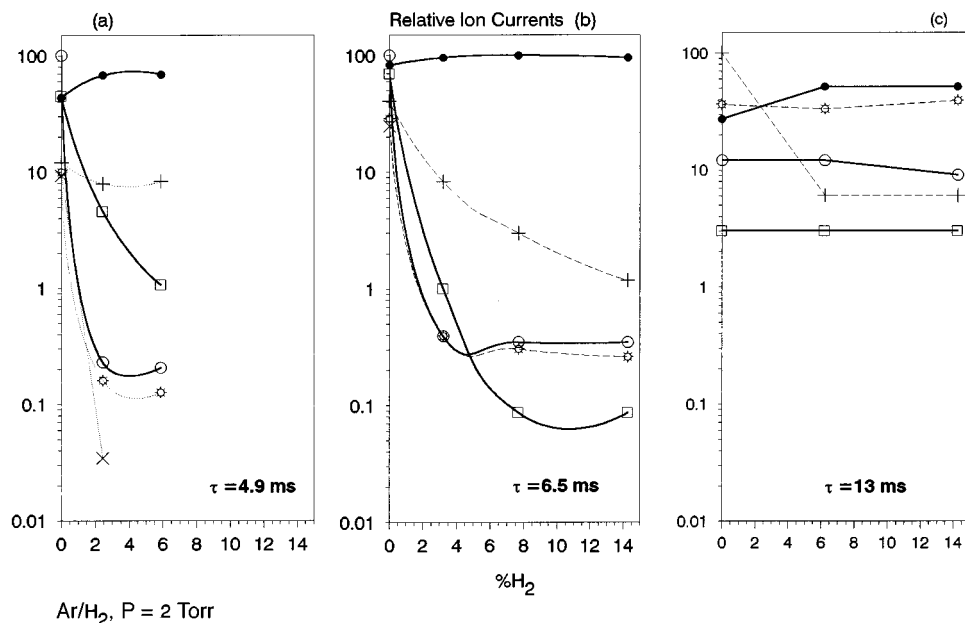


FIG. 6. Relative intensities (logarithmic scale) of ions versus H_2 (percent of the Ar flow rate) added at the downstream port, when $P_2 = 2$ Torr, $V_{\text{dis}} = 800$ V, and $C_{\text{dis}} = 2.1$ mA, and at $\tau (V_1) =$ (a) 4.9 (400), (b) 6.5 (300), and (c) 13 (150) ms (ml min^{-1}). \circ , Ar^+ ; \square , ArH^+ ; \bullet , $^{63}\text{Cu}^+$; \times , H_2O^+ ; \star , H_3O^+ ; \odot , Ar_2^+ .

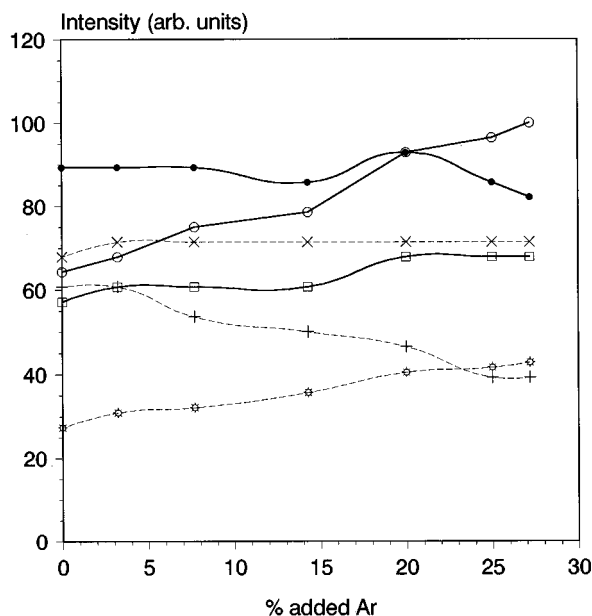


FIG. 7. Relative intensities (normal scale) of ions versus Ar (percent of the Ar discharge gas flow rate, $V_1 = 300 \text{ ml min}^{-1}$) added at the downstream port, when $P_2 = 2 \text{ Torr}$, $\tau = 6.5 \text{ ms}$, $V_{\text{dis}} = 800 \text{ V}$, and $C_{\text{dis}} = 2.1 \text{ mA}$, \circ , Ar^+ ; \square , ArH^+ ; \bullet , $^{63}\text{Cu}^+$; \times , H_2O^+ ; $+$, H_3O^+ ; \ast , Ar_2^+ .

fore also been calculated using the theoretical k_L value.

The actual concentrations of H_2O and Cu in the flow tube are not known. Sputtered Cu atom concentrations close to the cathode must be very high in order to get a significant ion peak in the mass spectrum, but this will drop off down the flow tube due to radial diffusion and condensation on the tube walls. For guidance the k'_1 , k'_7 , and k'_{10} values are given for two extreme concentrations of Cu : 1 and 10^4 ppm. The k' values for reactions involving water are based on the certified moisture content of the Ar gas used. These values could be an underestimate, however, because [14] of the difficulty of excluding degassing from the gas lines and outgassing from the sputter heated cathode sample and probe head.

In previous mass spectrometer studies [4,15,21] of the ions from the negative glow it has been assumed that the bulk of ionization results from direct electron impact and subsequent ion-molecule reactions. However, it is well known that the Ar discharge is an intense source of the $\text{Ar}(^3P)$ metastable states [22] and this is a likely precursor particularly of ions of sputtered metal atoms [23–26]. It was shown by Ferreira, Laureiro, and Ricard [10] that stepwise ionization via metastable states could also be important in a low-pressure argon positive column. The states considered by these and subsequent authors were the two $\text{Ar}(^3P)$ and the two resonance levels. The experiments of Pichanik and Simpson [27] demonstrate that in fact a whole cascade of higher metastable excited states, in addition to $\text{Ar}(^3P)$, are likely to be created by the broad spectrum of electron energies in the discharge. Many of these are likely to be above the ionization energy of Ar. Although little studied, there is a relatively high cross section for the formation of autoionizing states of Ar by low-energy electron impact and they are metastable [28] with lifetimes greater than 10^{-6} s. These are optically forbidden states thought to be caused by excitation

of the $3s$ rather than the $3p$ electrons, with resonances in the region from 20 to 40 eV, e.g. [29], singlet and triplet states: $(3s3p^64s) ^1S$ at 25.8 eV, $(3s3p^64p) ^1P$ at 26.7 eV, and $(3s3p^63d) ^1D$ at 27.55 eV. Resonances have been reported even at very high electron energies [30]. There is little, if any, information concerning the reactions of higher excited states of Ar. On the other hand, the $\text{Ar}(^3P)$ and $\text{Ar}(^1P)$ levels have been studied extensively [22–26,31,32]. They obviously [31] accumulate by collisional and radiative cascades from these higher states. Their collisional quenching rate by Ar is very slow at 1 Torr compared [31,32] to that by H_2 .

In the positive column at least, neutral ionization reactions rather than direct electron impact are thought to be important [10,11,22]. A summary of important reactions mainly involving $\text{Ar}(4s)$ atoms has been drawn up by Karoulina and Lebedev [11] for example and an adapted version is given in Table II. Presumably these could be extended to involvement of higher levels, when they are sufficiently concentrated.

Net removal of ions from the system occurs either by ambipolar diffusion and discharge at the walls and/or by electron-ion recombination. The latter is very slow for atomic ions, but very efficient for molecular species [33]. The rate coefficients in Table I are based on the assumption that the electron temperature is thermal. At higher energies the values decrease. Ion relaxation by ambipolar diffusion is characterized [34] by the diffusion loss coefficient λ , which is directly dependent on the ambipolar diffusion coefficient D_a and inversely dependent on pressure and the square of the “diffusion length” (defined by the geometry of the apparatus). Smith and Cromey [35] have measured D_a (Ar^+ in Ar) in the afterglow of a discharge at 300 K to be $55 \text{ cm}^2 \text{ s}^{-1} \text{ Torr}$. The diffusion process is slowed down for ions in the presence of their parent gas because [34] of resonant charge transfer (Ar^+/Ar) or symmetrical proton transfer (ArH^+/Ar). It is therefore expected to be faster for the other ionic species.

The tabulated data are for thermal reactions, whereas the charged species in a plasma are not thermal. Nevertheless, they serve to indicate the reactions that should be considered to help rationalize the chemistry.

B. Reactions without the addition of H_2

The main features of the residence time spectra in Figs. 3 and 4 are in accord with the presence of water impurity and sputtered Cu in the Ar gas. Hence the major ions are Ar^+ , ArH^+ , and Cu^+ at short residence time, minor ions being H_3O^+ , Ar_2^+ , and H_2O^+ . This is very similar to the studies of “static” glow discharge ion sources [4,15,21]. Possible ion-molecule reactions contributing to the ion population are therefore the usual candidates outlined in Table III. Of these only Ar^+ has no potential ionic precursor. If ion-molecule processes only are assumed, its decay rate should be Eq. (4), where n_e is the electron number density, and t is the reaction time,

$$-\frac{\partial[\text{Ar}^+]}{\partial t} = \sum k' = k_1[\text{Cu}] + k_2[\text{H}_2\text{O}] + k_{13}n_e + \lambda_{\text{Ar}^+}. \quad (4)$$

TABLE I. Exothermic ion-molecule reactions possible in the glow discharge plasma (all in Ar at 1 Torr and 303 K, when $n/V=3\times 10^{16}$ molecules cm^{-3}), containing Ar, sputtered Cu, trace H_2O , and added H_2 .

Reaction number	Reaction $-\Delta H$ (kJ mol $^{-1}$) ^a	k^b (10^{-10} cm 3 s $^{-1}$)	k'^c (s $^{-1}$)	k_L^d (10^{-10} cm 3 s $^{-1}$)
1	⁷⁷⁵ $\text{Ar}^+ + \text{Cu} \rightarrow \text{Ar} + \text{Cu}^+$		$36^{e,1}$ 3.6×10^{5f}	12
2	⁸¹ $\text{Ar}^+ + \text{H}_2\text{O} \rightarrow \text{ArH}^+ + \text{OH}$	13	78^g 312^h	8
3	³⁰⁴ $\text{Ar}^+ + \text{H}_2\text{O} \rightarrow \text{Ar} + \text{H}_2\text{O}^+$			
4	¹⁴⁴ $\text{Ar}^+ + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H}$	8, 9	1.35×10^{6i}	15
5	³³ $\text{Ar}^+ + \text{H}_2 \rightarrow \text{Ar} + \text{H}_2^+$			
6	¹²³ $\text{Ar}^+ + 2\text{Ar} \rightarrow \text{Ar}_2^+ + \text{Ar}$		313^j	
7	²⁸⁹ $\text{ArH}^+ + \text{Cu} \rightarrow \text{Ar} + \text{CuH}^+$			
7'	¹⁹⁵ $\rightarrow \text{Ar} + \text{Cu}^+ + \text{H}$		$36^{e,1}$ 3.6×10^{5f}	~ 12
8	³²⁶ $\text{ArH}^+ + \text{H}_2\text{O} \rightarrow \text{Ar} + \text{H}_3\text{O}^+$	20	120^g 480^h	~ 8
9	⁵² $\text{ArH}^+ + \text{H}_2 \rightarrow \text{Ar} + \text{H}_3^+$	0.3	4.5×10^{4i}	~ 15
10	¹⁴³ $\text{H}_3^+ + \text{Cu} \rightarrow \text{H}_2 + \text{Cu}^+ + \text{H}$		$102^{e,1}$ 1×10^{6f}	34
11	²⁷⁴ $\text{H}_3^+ + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_3\text{O}^+$		$13.5^{g,1}$ $54^{h,1}$	18
	Recombination	k, m		
12	$\text{Cu}^+ + e^- \rightarrow \text{Cu}$	1 – 0.01		
13	$\text{Ar}^+ + e^- \rightarrow \text{Ar}$	1 – 0.01		
14	$\text{ArH}^+ + e^- \rightarrow \text{Ar} + \text{H}$	~ 1000		
15	$\text{H}_2\text{O}^+ + e^- \rightarrow \text{H}_2\text{O}$			
16	$\text{Ar}_2^+ + e^- \rightarrow 2\text{Ar}$	9100		
17	$\text{H}_3^+ + e^- \rightarrow \text{H}_2 + \text{H}$	2300		
18	$\text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2\text{O} + \text{H}$	6300		

^aValues calculated from the data in Ref. [41].

^bValues taken from the data in Ref. [42].

^cPseudo first-order rate constant equal to k (molecule).

^d $k_L = 2\pi e(\alpha/4\pi\epsilon_0\mu)^{1/2} = 2.338 \times 10^{-15}(\alpha/\mu)^{1/2}$ cm 3 s $^{-1}$, where α is polarizability in units of 10^{-24} cm 3 and μ is the reduced mass in units of g mol; see Ref. [18].

^eAssuming 1 ppm [Cu].

^fAssuming 1% [Cu].

^gAssuming 1 ppm [H_2O].

^hAssuming 4 ppm [H_2O].

ⁱAssuming 5% H_2 in Ar.

^jTaken from Ref. [35].

^kValues taken from Ref. [33].

^lUsing k_L values.

^mAssuming all electrons are thermal.

TABLE II. Formation and removal of excited states of Ar and possible [9] indirect ionization processes in the Ar discharge plasma. Ar^{**} and Ar^{*} represent unspecified excited states of Ar above the Ar(4s) levels and Ar^M and Ar^R are the ³P and the resonance levels of Ar(4s), respectively; Q is a quenching gas.

Reaction number	Reactions	$k/10^{-9}$ (cm ³ s ⁻¹)	Work
19	$\text{Ar} + e \rightleftharpoons \text{Ar}^{**}, \text{Ar}^*, \text{Ar}^M, \text{Ar}^R + e$		
20	$\text{Ar}^M + e \rightleftharpoons \text{Ar}^R + e$	235 310	Ref. [11]
21	$\text{Ar}^{**} (+ \text{Ar}, \text{Ar}^*, \text{etc.}) \rightarrow \text{Ar}^+ + e + \text{Ar}$		
22	$\text{Ar}^{**}, \text{Ar}^*, \text{Ar}^M, \text{Ar}^R + \text{Ar}^{**}, \text{Ar}^*, \text{Ar}^M, \text{Ar}^R \rightarrow \text{Ar}^+ + \text{Ar} + e$	1-2	Ref. [43]
23	$\rightarrow \text{Ar}_2^+ + e$		
24	$\text{Ar}^{**}, \text{Ar}^*, \text{Ar}^M, \text{Ar}^R + Q \xrightarrow{\text{collisional quenching}} \text{Ar} \text{ (lower excited or ground state)} + Q^*$		
25	$\text{Ar}^*, \text{Ar}^M, \text{Ar}^R \xrightarrow{\text{diffusion to walls}} \text{Ar}$		Ref. [11]

If the ions all originated at the discharge (i.e., close to the cathode), then the ion currents would all decay as the residence time increased because of reaction, radial diffusive loss to the tube walls, and recombination. All other things being equal, this would be an exponential (first-order) decay (and hence a straight-line plot in Fig. 3). However, it is clear from both Figs. 3 and 4 that the Ar⁺ decay is not first order. At 1 Torr (Fig. 3), in the range 3.5 < τ < 6 ms the decay is relatively steep, but thereafter slows down. This behavior is consistent with the decrease in afterglow plasma density at longer residence times, which can have two effects. The first is a decrease in losses by electron recombination because of a reduction in [n_e]. The second is a possible change from ambipolar to the slower free diffusion process. If reaction 1 were to be important, a third complication is the depletion of [Cu] with increasing τ because of its radial diffusion to and condensation on the walls.

At earlier residence times (τ < 3.5 ms in Fig. 3 and τ < 6 ms in Fig. 4) the Ar⁺ decay rate slows down significantly. This indicates that there must be a significant non-ionic source of Ar⁺ to offset the losses. In the past it has been presumed that the ionization of Ar in the negative glow of the discharge is mainly by direct electron impact [15]. The discharge conditions do not change here and therefore there

TABLE III. Ion-molecule reaction scheme, that would lead to products observed in the discharge. Ar^M denotes metastable Ar(4s) atoms.

Reaction identifier	Reactions
2	$\text{Ar}^+ + \text{H}_2\text{O} \rightarrow \text{ArH}^+ + \text{OH}$
8	$\text{ArH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Ar}$
(g)	$\text{Ar}^M + \text{Cu} \rightarrow \text{Cu}^+ + \text{Ar} + e$
1	$\text{Ar}^+ + \text{Cu} \rightarrow \text{Cu}^+ + \text{Ar}$
7	$\text{ArH}^+ + \text{Cu} \rightarrow \text{Cu}^+ + \text{Ar} + \text{H}$
26	$\text{Ar}^+, \text{ArH}^+, \text{H}_3\text{O}^+, \text{Cu}^+ \rightarrow \text{loss by diffusion and recombination}$

is no reason to suppose any significant changes in electron energy, for example, which might affect the process of direct ionization by electron impact. In addition, the energy of electrons so far down the flow tube is unlikely to be high enough for this form of ionization to be significant. The alternative is indirect processes as suggested [10,11,22] for positive column processes previously. It is possible, therefore, that long-lived excited Ar metastable states may be contributing. Higher excited states might autoionize or undergo associative ionization within the flow tube in the vicinity of the ion exit.

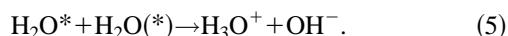
The other principal ions also decay with increasing τ, but at slower overall rates. However, these all have potential ionic precursors. Thus it is clear that at relatively short reaction times Cu⁺ is also still being formed down the flow tube and to a greater extent than Ar⁺. This could occur through ion-molecule reactions 1 and/or 7 or Penning ionization, reaction (g) of Table IV.

At 1 Torr H₃O⁺ increases in absolute intensity (Fig. 5), going through a maximum at about 5 ms. Although reaction 8 could be the prime source of H₃O⁺, the behavior at longer residence times again suggests the involvement of a neutral source. The major ions, by orders of magnitude at τ > 6 ms, are Cu⁺ and H₃O⁺. There is no mechanism by which Cu⁺ could react with water to form H₃O⁺ and yet H₃O⁺ continues to increase relative to Cu⁺ and becomes

TABLE IV. Proposed reaction scheme for the population of ions in the discharge afterglow by neutral processes.

Reaction identifier	Formation of Ar ⁺ , ArH ⁺ , and Cu ⁺
(a)	$\text{Ar}^{**} + \text{Ar} \rightarrow \text{Ar}^+ + e$
(b)	$\text{Ar}^{**} + \text{H}_2 \rightarrow \text{Ar}^* + \text{H}_2 \text{ (or } 2\text{H?)}$
(c)	$\text{Ar}^* + \text{Ar}^* \rightarrow \text{Ar}^+ + \text{Ar} + e$
(d)	$\text{Ar}^* + \text{H}_2\text{O} \rightarrow \text{ArH}^+ + \text{OH}$
(e)	$\text{Ar}^* + \text{H}_2 \rightarrow \text{ArH}^+ + \text{H} + e$
(f)	$\text{Ar}^* + \text{H}_2 \rightarrow \text{Ar}^M + \text{H}_2^* \text{ (or } 2\text{H?)}$
(g)	$\text{Ar}^M + \text{Cu} \rightarrow \text{Ar} + \text{Cu}^+ + e$

dominant at $\tau > 8$ ms. Apart from anything else this shows that recombination is not an important process at these long residence times because the very high recombination rate coefficient for H_3O^+ compared to that expected for Cu^+ (slow because it is atomic) would favor the latter. It is possible that, despite its larger mass, Cu^+ has a faster diffusive loss rate than H_3O^+ . This could occur, for example, if symmetrical proton transfer with water is important, compared to resonant charge transfer from Cu. However, the levels of both Cu and H_2O are very low compared to Ar. An alternative is that H_3O^+ has a longer-lived neutral source than Cu^+ . This must be an excited H containing molecule. Water is known [36] to quench excited Ar atoms and could therefore readily become excited itself (in addition to any chemical reactions induced). Hence reaction (5) is a possible source and was suggested before [4]. Although there is no specific proof of this reaction, it will be seen that the effect of adding H_2 to the system does concur with the proposition that the source is a neutral reaction (*vide infra*):



The minimum excitation energy required to drive this reaction is 7 eV. H_2O^+ , always a very minor ion, also reaches a peak, but at 4–4.5 ms, just ahead of H_3O^+ .

In addition, there are two possible routes to the formation of Ar_2^+ : the neutral reactions, 23 of Table II, and the ion-molecule reaction, 6 of Table I. Gaur and Chanin [37] found that the neutral (Hornbeck-Molnar) reaction is more important at the pressures used in these experiments, in agreement with the implications of Knewstubb and Tickner's data. [4] In Fig. 5 this ion also rises to a maximum at $\tau = \sim 5$ ms when $P_2 = 1$ Torr. This is suggestive of a connection between the three, perhaps involving the same excited states of Ar, as a precursor.

Based on the above evidence alone, it is concluded that the ions observed probably have neutral ionization sources in addition to any direct ionization or ion-molecule reactions involved. However, it will be seen from the addition of H_2 experiments that almost all ions observed under faster flow conditions are created from neutral precursors.

C. Reactions with the addition of H_2

1. Ion-molecule reactions

In Fig. 5, where at 0% H_2 $\text{Ar}^+ \gg \text{ArH}^+ \approx \text{Cu}^+$, it appears as if ArH^+ is formed from Ar^+ when H_2 is added. This is of course the expected product of the Ar^+/H_2 reaction 4. It then appears as if Cu^+ is being formed from ArH^+ . The reaction of ArH^+ with Cu can only occur via 7 or 7'. CuH^+ was detected, but at levels less than 0.2% of Cu^+ , suggesting that dissociative proton transfer 7' might be the main product of this interaction. However, the results of adding H_2 under slow flow rate conditions [Fig. 6(c) $P_2 = 2$ Torr, $\tau = 13$ ms] show that ion-molecule reactions involving H_2 are not important in these experiments. For example, were this a significant factor in the removal of Ar^+ by reaction 4, then the relative rate of removal should be at least as fast as when H_2 is added under fast flow rate conditions [Fig. 6(a)]. In fact, there is no significant effect on Ar^+ (or indeed ArH^+) signals when H_2 is added to the system at long residence

time. This may seem odd given the fast pseudo-first-order rate constant for a 5% addition of H_2 at 1 Torr. However, it should be remembered that the time available for reaction with H_2 is much shorter than τ because it is added directly in front of the ion exit and swept rapidly downstream.

Furthermore, as shown in Figs. 6(a) and 6(b), when the starting conditions are different, when H_2 is added the ArH^+ (created by reactions with trace water) is only quenched, and at a very much higher rate than the increase in Cu^+ (note that Fig. 6 has a logarithmic scale compared to Figs. 5 and 7). Hence any relationship between the two ions is not direct. Clearly reaction 7 or 7' therefore is not the important sink mechanism for ArH^+ as might be inferred from the data in Fig. 5. The main *chemical* removal process expected for ArH^+ in the presence of 1% or more of H_2 ought to be the formation of H_3^+ by proton transfer to H_2 (reaction 9). Even though this is a relatively inefficient reaction, the high H_2 levels make this very fast by comparison with 8 the pseudo-first-order reaction with H_2O (the main ion-molecule reaction sink of ArH^+ in "pure" Ar). Dissociative proton transfer 10 to Cu from H_3^+ could then ensue. However, the relative rate coefficients are such that a high steady-state level of H_3^+ would still be expected to appear. In fact $[\text{H}_3^+]$ and $[\text{H}^+]$ are generally less than 0.2% of $[\text{Cu}^+]$ or $[\text{ArH}^+]$ signals, even at very high H_2 additions (see Fig. 5). KT reported [4] being unable to find H_3^+ . The overall behavior is therefore not consistent with formation and removal by known ion-molecule reactions.

2. Recombination

Most authors [5,7–9] have ascribed the quenching effect by H_2 in discharge plasmas to enhanced ion recombination. Gordon and Kruger [5] argued it is caused by the formation and interaction of H atoms that act to quench $\text{Ar}(^3P)$ down to the ground state. This was thought to be effective in removing electrons where there is an overpopulation of the excited Ar atoms because three-body Ar^+ recombination is much faster where the third body is a ground-state Ar atom. If this mechanism were applicable here, then our addition of ground-state Ar downstream (Fig. 7) might be expected to have a similar effect to the addition of H_2 . In fact, the opposite is observed, in that Ar^+ increases (while Cu^+ is affected only slightly).

Meulenbroeks *et al.* investigated [6] both charge density and optical emission variations in a plasma jet of Ar, with and without the addition of H_2 . They argue (*vide supra*) that the severe depletion of charge in the Ar/H_2 afterglow is caused by reaction 4 and the conversion of Ar^+ , which has a low recombination coefficient, to ArH^+ , which has a very high value and is therefore rapidly removed in reaction 14, taking away electrons in the process.

While the plasmas investigated above were produced under rather different conditions, the experimental effects seem to be similar to that demonstrated here. However, recombination cannot provide the explanation for our data. The main observation that discounts it is that in our systems ArH^+ is produced in abundance in the absence of H_2 , by interactions with trace water, and it is one of the most prominent peaks before H_2 is added, under the same flow and discharge conditions. For ion-electron recombination to be significantly

enhanced would therefore require a significant increase in the density of electrons in the afterglow, somehow caused by the presence of H_2 . Yet when H_2 is added downstream, as here, there is very little ionization of the H_2 and there is no change in the discharge current. Furthermore, H_3O^+ has an even higher recombination coefficient than ArH^+ , yet in Fig. 6(a) the H_3O^+ signal remains relatively unaffected by the addition of H_2 when Ar^+ and ArH^+ are both severely quenched. The fact that the Cu^+ signal is enhanced is a significant pointer to the probable mechanism.

3. Neutral ionization reactions and quenching of metastable states

Penning ionization from $\text{Ar}(^3P)$, the lowest metastable state of Ar, is thought [23–26] to be a significant source of the ionization of sputtered metal atoms in a glow discharge. In our experiments the Cu^+ is boosted significantly by the addition of H_2 . Since it has been shown above that ion-molecule reactions are not directly responsible, it is reasonable to explore the possibility that the effect is created by boosting the $\text{Ar}(4s)$ levels. Equally ion-molecule reactions and recombination have both been discounted as the cause of the loss of Ar^+ . There are two remaining possibilities. One is that the precursors to these ions are also mainly non ionic i.e., they must be excited Ar atoms, and it is these that are quenched by H_2 . If they are above the $\text{Ar}(4s)$ levels and H_2 promotes the collision cascade downward resulting in the net population of $\text{Ar}(4s)$, then this would boost the Cu^+ signals while removing the other ions from the mass spectrum. The initial populations of the highest excited states, prior to H_2 addition, will obviously depend on the time allowed for the energy distribution to have relaxed beforehand. This can then help explain the difference in behavior between the short residence time experiments at lower pressures and that at longer residence times and higher pressures.

The second possibility, as suggested by KT [4], is that the presence of H_2 lowers the electron temperature and thereby diminishes the extent of ionization by direct electron impact. However, (a) the momentum transfer cross sections [38] for H_2 are actually slightly less than that for Ar, (b) there is no H_2^+ and very little H^+ formed even when small amounts of H_2 are added, and (c) this mechanism would not explain the increase in Cu^+ . Although the overall electron impact ionization efficiency for H_2 is about 0.29 times that for Ar, the ionization energy is lower. The absence of the ions of H_2 suggests that in any case, ionization by electron impact is not important in the region of the discharge sampled.

The series of reactions in Table IV are therefore suggested to account for the observations made and are described below. The mechanism is illustrated in Fig. 8.

4. Ar^+ , ArH^+ , and Cu^+

Although KT [4] concluded that an ion-molecule reaction of Ar^+ with H_2 or its dissociated form H was likely to be responsible for the formation of ArH^+ in the negative glow, they found that the results obtained in the positive column or Faraday dark space region were consistent with a neutral source of ion formation. In our experiments at $P_2=2$ Torr

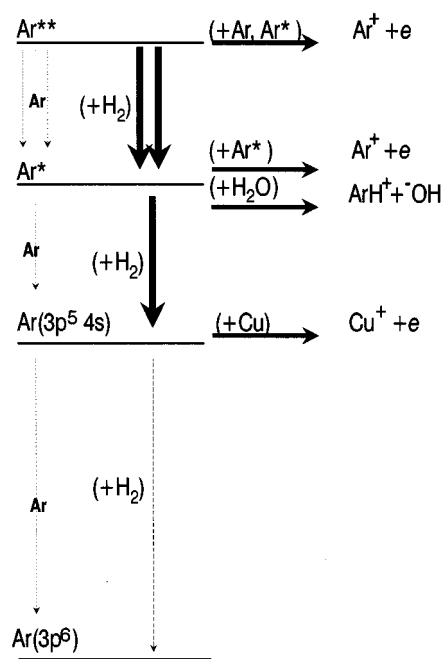


FIG. 8. Schematic diagram representing the proposed mechanism of ion formation and removal with the addition of H_2 , at early residence times in the discharge afterglow.

[Figs. 6(a) and 6(b)] ArH^+ is removed without a concomitant rise in credible ionic products (and hence is not removed effectively by an ion-molecule reaction; *vide supra*). This strongly suggests that ArH^+ is itself the product of a neutral reaction rather than an ion-molecule process, in which again it is the neutral precursor that is actually quenched by H_2 . Indeed, the fact that in Fig. 6 there is no increase in ArH^+ when H_2 is first added, which would be expected if the Ar^+/H_2 reaction 4 were a significant source, is also testament to this (the ArH^+ observed is the product of a reaction with trace water, not H_2). Furthermore, the quenching of ArH^+ production is ultimately more complete than for Ar^+ [Fig. 6(b)] which is again surprising if reaction 4 is important. In addition, although ultimately more complete, the rate of quenching is much slower. This is consistent with the associative ionization mechanism because H_2 quenching of Ar^* would have a much greater proportionate effect on Ar^+ than on ArH^+ . This is because the rate of Ar^+ production (Table IV, reaction c) is proportional to $[\text{Ar}^*]^2$, but the production of ArH^+ (reaction d) depends on $[\text{Ar}^*]$. Ultimately, however, the production of both will reduce to zero except for any ions carried through from upstream in the flow tube. They are reduced by a factor between 100 and 1000.

In Fig. 5 ($P_2=1$ Torr) the ionization processes in the discharge are being observed at a shorter residence time and the pressure is lower than in Fig. 6. Since there is less time and a lower collision frequency, the collision cascade in Ar will have had less time to operate. Therefore, the proportion of the higher-energy excited states will be greater. Here there is an initial rise in ArH^+ as H_2 is added. It then falls again, but the ultimate quenching of ArH^+ is small in comparison to Ar^+ , the reverse of above. This is rationalized (see Fig. 8) if more excited states, Ar^{**} , higher in energy than before, are

involved in the formation of Ar^+ but not ArH^+ . If, as H_2 is added, Ar^{**} is quenched by collisional cascading down the energy ladder, passing through Ar^* , energy states that do react (either with water or possibly H_2) to form ArH^+ , this ion will initially increase, but then decay again as further quenching removes Ar^* down to the lower states Ar^M ; which, as before, enhances the Penning reaction with Cu. The relative effect on Cu is all the greater because of the greater proportional switch in the populations of the higher-energy states to the lower metastable states, presumed to be the precursors of Cu^+ . While Ar^+ is almost completely quenched as before, ArH^+ is reduced relatively little overall because the quenching process down to Ar^* itself provides a source for the ArH^+ .

H_2 , while quenching the upper states of Ar, Ar^* , etc., results in a net increase in the population of the lower metastable states, within the time scale of our experiments. This is despite the fact that H_2 also quenches $\text{Ar}(^3P)$ [31,32]. This requires that $k_q^{**} \gg k_q^{3P}$, where k_q are quenching rate coefficients.

5. Ions formed upstream in the flow tube

Ions must be formed continuously down the flow tube by either ionization or ion-molecule reactions. These ions, if carried down the flow tube, would normally be expected to form a strong base line of ion intensity in the mass spectrum, unaffected by H_2 except for ion-molecule reactions. Therefore, the fact that the degree of quenching of Ar^+ and ArH^+ in the recorded spectra is so complete for the faster flows, without a concomitant increase in other ions to replace them indicates that few of the ions created upstream reach the ion exit. This must be caused by a net negative field gradient in the direction of the cathode over most of the distance between the ion exit and the cathode pin, when the plasma density is high. There is a short negative fall due to the sheath potential close to and in the direction of the anode surface [39]. Hence, at the faster flow rates ions sampled at the ion exit cone (with a small voltage applied) are mainly those formed at this point, despite the flow of gas. The application of a large ion extraction voltage enhances signal intensities tenfold, with changes in the relative ion intensities consistent with their formation at shorter residence times (i.e., further upstream in the flow tube), as expected.

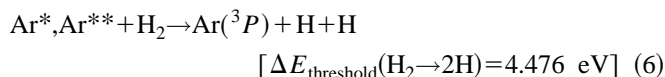
6. H_3O^+ and Ar_2^+

At the slowest flow rates [Fig. 6(c)] most ions observed were probably created upstream in the flow tube. They are therefore affected little by the addition of H_2 , except for H_3O^+ . This is readily quenched to 6% of its abundance by less than 5% H_2 . Since there are no credible ion-molecule reactions of H_2 with H_3O^+ this again points to a very long-lived neutral excited precursor, as suggested earlier.

Ar_2^+ is well known as a product of excited neutral reactions, as discussed above. Its behavior with respect to H_2 addition follows closely on that of Ar^+ .

D. Energy transfer

The main criterion for efficient energy transfer is usually energy resonance between the quencher and quenched species. Electronically excited states of H_2 are greater than 11.28 eV above its ground state. Therefore, if electronic-to-electronic energy transfer occurs it must involve states of Ar greater than 22.8 eV in energy, coinciding with the region of argon's autoionizing states. At lower energies quenching must involve rovibrational or dissociative energy transfer such as reaction (6). Noble gas discharges containing small percentages of H_2 are well known as high-intensity sources of H atoms in flow systems



(see Ref. [40]).

V. CONCLUSION

Ionization in the plasma of a dc glow discharge has been studied using a fast flowing GD ion source mass spectrometer, with the facility to mix in gases close to the ion exit, without interfering with the discharge. Reactive processes can therefore be studied as a function of time. The significant ions using a Cu cathode were found to be Ar^+ , ArH^+ , Cu^+ , and H_3O^+ , the H containing ions arising from reactions with trace water. This is similar to previous studies on static systems. It was found here that the addition of H_2 causes a dramatic quenching of all ions except for Cu^+ , which is enhanced. It has been shown that this cannot be consistently explained by either electron cooling, ion-molecule, or recombination reactions as previously suggested. However, the mechanism can be explained in terms of the effect of the H_2 on excited metastable states, significantly higher in energy than the normally assumed $\text{Ar}(^3P)$ levels. It is argued that H_2 rapidly quenches these states down to the $\text{Ar}(^3P)$ level, thereby removing the precursors to Ar^+ and ArH^+ , but boosting the precursors to Cu^+ formation by the Penning reaction.

The ions sampled are only those formed close to the ion exit. The implications are that (a) the discharge contains very high concentrations of long-lived high excited states of Ar, which increases significantly towards the negative glow, and (b) neutral ionization processes, other than reactions involving $\text{Ar}(^3P)$ or $\text{Ar}(^1P)$, are important outside the cathode fall region of the discharge compared to direct ionization and ion-molecule reactions. Such states are not normally considered in models of these systems. The loss of ionization is very similar to that observed previously, by different means, and indeed under different discharge conditions. The present findings may therefore have a bearing on the mechanistic interpretation of the previous published experiments.

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