Diagnostics of microwave plasmas of C_2H_2: Mass spectrometric investigations of ionic and neutral species

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The determination of the ionic and neutral chemical components of the flowing microwave (MW) discharge plasma of acetylene was performed by Li^+-ion-attachment mass spectrometry. Plasma composition was investigated as a function of controllable parameters such as the C_2H_2 flow rate (pressure), the microwave-induced power input, and the MW cavity position. The reaction schemes for some products are considered, particularly with regard to the role of radical and ionic condensation reaction processes. An attempt was made to link both the ionic and neutral species to a proposed mechanism. A model that explains the observed phenomena and that is consistent with the dependence on plasma parameters is suggested. The model's predictions indicate that, for example, the principal ionic condensation reaction can be summarized by the reaction sequence $C_nH_2^+ + C_2H_2 \rightarrow C_{n+2}H_2^+ + H_2$ ($n=2,4,6,8$), while reactions involving a hydrogen atom may lead to the formation of neutral C_mH_n ($n>m$) species, such as C_2H_3, C_3H_4, and C_4H_5. [S1063-651X(98)01711-5]

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I. INTRODUCTION

For many years there has been considerable interest in studying C_2H_2 chemistry in low-pressure electrical discharges at the molecular level [1–3] because of its application in plasma polymerization for depositing thin films [4,5]. Fundamental investigations began in the mid 1960s [6,7] and today are rapidly developing into a research field that includes a host of optical spectroscopic and mass spectrometric product analyses.

In a study of dc discharge through C_2H_2, Smith *et al.* [8] identified a variety of linear conjugated molecular products: carbon atom chains C_n ($n=2-9$) and polyacetylene radical cations $H-(C \equiv C)_n-H^+$. In suggesting that free radicals are the major reactive species in the glow-discharge polymerization process, Kobayashi, Bell, and Shen [4] are in disagreement with Vasile and Smolinsky [9], who concluded that reactions of $C_2H_2^*$ and ionic condensations leading to polymeric products may well dominate the chemistry of the discharge.

Several workers, including some astrophysicists [10,11], have reported the presence of additional chemical groups in C_2H_2 electrical discharges. For instance, Fujii [12] reported the unexpected formation of many unfamiliar HC neutral products, among which are various free radicals such as C_nH_3 ($n=2,4$), C_nH_5 ($n=2,4,6$), and C_nH_7 ($n=3,4$). Researchers still disagree on reaction mechanisms: Both cationic and free radical mechanisms have been proposed to predominate. Curiously, no one has yet considered a combined mechanism, despite evidence that both ions and radicals are involved. Clarification of this basic problem is needed.

In contrast, the study of shock-tube pyrolysis [6,7,13], photolysis [14–16], and chemical ionization [17,18] of C_2H_2 has been extensive. A microwave (MW) gas discharge is not

strictly comparable or analogous to the experimental situations existing in any of these cited studies, but a gas discharge can be looked on as a composite of many of the processes existing in each study. The results of these studies have proved to be extremely helpful in explaining our observed results. Therefore, the wealth of data available should be used in interpretating the present MW discharge work.

Our development of Li^+-ion-attachment mass spectrometry [19,20] has been shown to be a useful technique for determining both neutral and ionic transient species simultaneously [21]. In previous C_2H_2 studies [12], neutral polyacetylenes of the form $H-(C \equiv C)_n-H$ ($n=1-6$) were prepared and their mass spectra were measured. A natural extension would be to study large polyacetylene cations and to compare them with the neutral species in the plasma. A knowledge of both neutral and ionic species would enable C_2H_2 MW plasma to be understood. Information on complex reaction processes would result when all the plasma species were evaluated.

This study was carried out to determine plasma species (including radical species) and a possible scheme for their formation, to establish the relative importance of neutral and ionic process in the MW discharge of C_2H_2. Densities were evaluated as a function of C_2H_2 gas flow rate, MW power input, and distance from the MW cavity. Flow tube studies were performed under various conditions with Li^+-ion-attachment techniques.

II. EXPERIMENT

A detailed description of the experimental setup can be found elsewhere [19–21]. We shall briefly review the main points here and describe changes made for this study.

Lithium ions were produced by heating a glass bead (Li^+ emitter) that contained lithium oxide in an aluminosilicate matrix. Emissions produced by the discharge gradually decreased. This decrease corresponds to a decrease in the adduct production of about the same magnitude. Emissions gradually increased again in proportion to the time the dis-

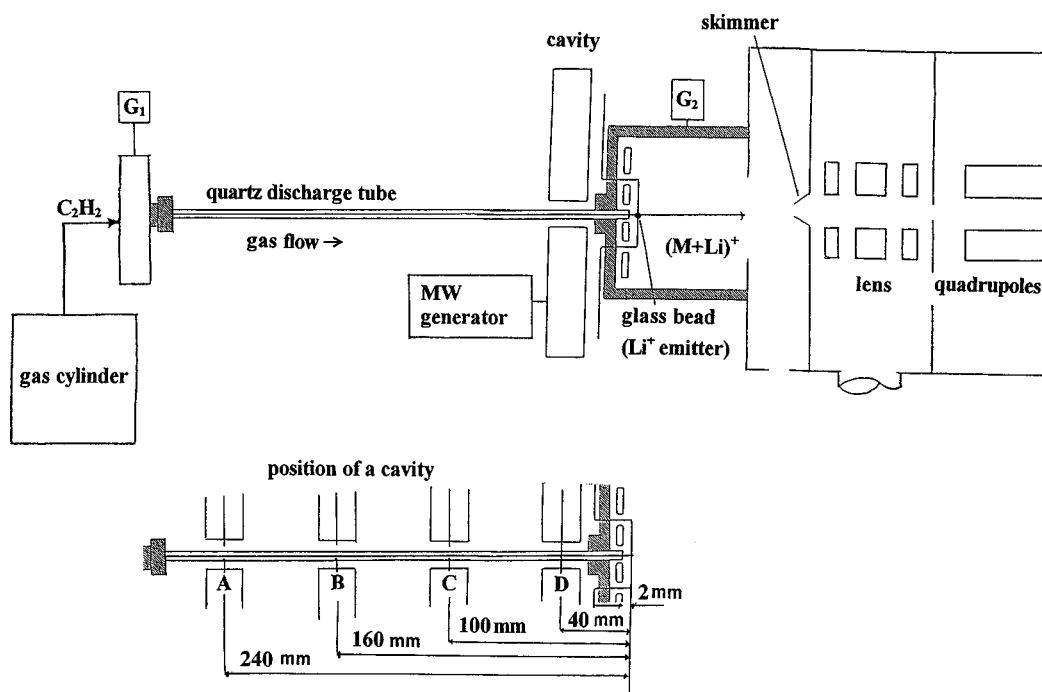*Electronic address: t-fujii@nies.go.jp

FIG. 1. System setup. Four positions of a microwave cavity were examined: upstream (A), central (B and C), and downstream (D). G_1, convectron pressure gauge; G, Pirani pressure gauge.

charge was off. Thus most mass spectrum analyses were done in terms of $F(\Sigma I)$ for each mass peak, where $F(\Sigma I)$ represents the normalized fractional concentration of each mass-to-charge ratio (m/z) considered. All the data points in the graphs were determined by averaging several repeated measurements. The coefficients of variation in the data for these runs were within $\pm 18\%$ at the 95% confidence level.

The MW source (Fig. 1) was constructed from a straight quartz tube (4 mm inner diameter, 6 mm outer diameter, 30 cm long). The C_2H_2 gas flowed down the tube. The MW plasma was created by connecting a cavity to a 2.465-MHz MW generator through a matching network. The cavity could be moved along the flow tube. The products sampled at D in Fig. 1 had the least opportunity to undergo reactions between formation and being sampled.

Mass spectra were obtained in either the presence (A) or absence (B) of Li^+. The intensity of any mass peak in A was subtracted from the corresponding mass peak in B to give the Li^+ adducts of particular neutral products. Mass spectra were measured downstream of the microwave cavity and the presence of free radicals in the plasma was determined. Mass was measured and peak height of $F(\Sigma I)$ was determined for each mass peak. The mass resolution was set at unit resolution. No attempt has been made to correct for the mass dependence of the mass spectrometer. The plasma composition was investigated as a function of the following parameters: MW cavity position (A, B, C, and D), C_2H_2 gas flow rate in the flow tube (1–16 mL/min) (the flow tube pressure at the upstream was correspondingly varied between 213 and 6666 Pa), and MW power input (30, 60, and 120 W).

III. RESULTS AND DISCUSSION

A. Mass spectrum

Figure 2 shows a typical mass spectrum over the m/z range 20–150 obtained for the C_2H_2 plasma when the Li^+

emitter was on [Fig. 2(a)] and off [Fig. 2(b)]. As fragmentation can be assumed to be negligible [19,20], the additional peaks in Fig. 2(a) are attributed to ion attachment to genuine chemical-neutral species effusing from the plasma; the peaks in Fig. 2(b) are due to ionic species formed in the plasma. The ionic products from the plasma were detected mass spectrometrically. The presence of various neutral discharge products is denoted by an increase in the current of the Li^+ adduct ions.

Table I identifies a variety of products in the observed mass spectra and shows a marked difference between the mass spectra A and B. It shows two characteristic features of the ionic species: Ions containing odd numbers of carbon atoms are absent except for $C_3H_3^+$ and the discharge is efficient at producing radical polymeric cations. The four most prevalent ions sampled were $C_6H_4^+$, $C_8H_4^+$, $C_{10}H_6^+$, and $C_{12}H_6^+$. Mass spectra were present for cations of the form $C_{2n}H_2^+$ ($n=2,3,4,5$). Presumably these are cations of diacetylene ($HC_{2n}H^+$), which is a ubiquitous component of flames of various volatile hydrocarbons [22].

Our results agree with the results of Vasile and Smolinsky's rf gas discharge study [9] up to a m/z of 77. Table I compares the ionic species obtained from their axial sampling of an rf discharge (200 V on the electrodes, 13.3 Pa) with those obtained from the MW discharge shown in Fig. 2(b). A significant difference between their results and ours is in the distribution of ionic products: We detected larger polymer cations of the form $C_mH_n^+$ ($m=8,10,12,14,16$).

A comparison makes it clear that the ion chemistry of the acetylene discharge resembles the results of chemical ionization (high-pressure) mass spectrometry quite closely [17,18]. This indicates that the MW discharge and the electron impact in chemical ionization conditions would result in essentially the same reaction paths.

Various free radicals as well as stable polymer molecules were clearly present. The latter are classified as C_n (n
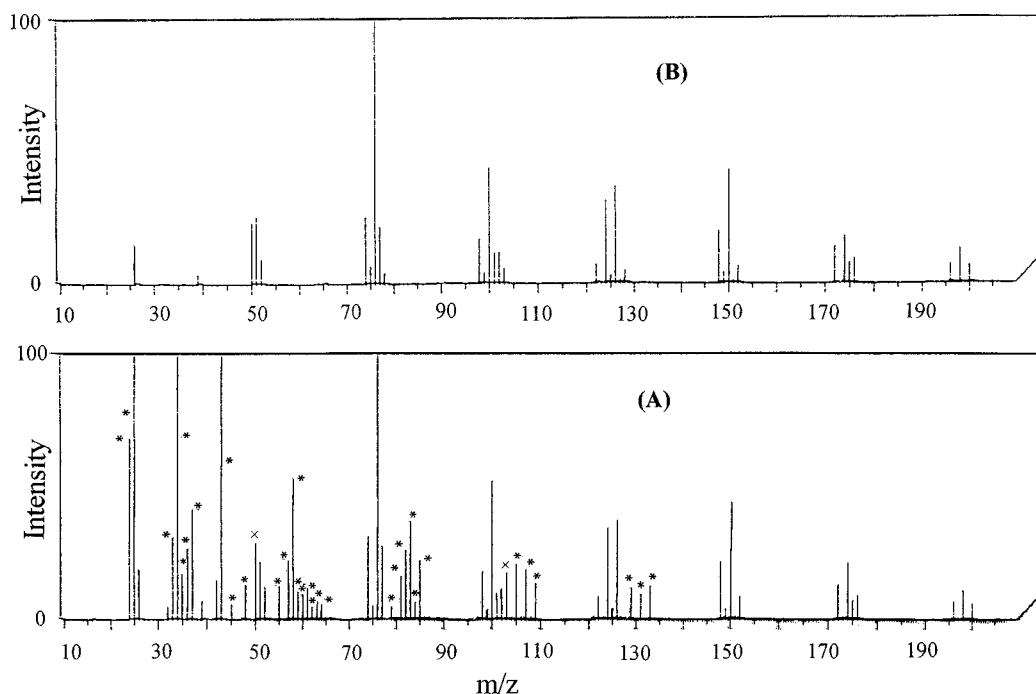
FIG. 2. Mass spectra of a 30-W, 840-Pa C_2H_2 MW discharge, at position C (flow rate 4 L/min) (a) sampled in the Li^+-on condition and (b) sampled in the Li^+-off condition (ionic species detection). Additional peaks in (a) due to Li^+ ion adducts are marked by $*$. The significantly increased peaks at m/z 50 and 103 in (a) consist of ionic species and Li^+ ion adducts. These are marked by x.

$=4,6,8$), C_nH_2 ($n=2,3,4,6,8,10$), C_nH_4 ($n=2,4,6,8,10$), and so on. Radicals such as C_nH_3 ($n=2,4,6$), C_nH_5 ($n=2,4,6$), C_nH_7 ($n=3,4$), and C_nH_9 ($n=4$) were detected. Some of them may be species having an aromatic ring, such as C_6H_4 and C_6H_6. Previous reports give data on neutral species where the experimental conditions were the same as here [12].

B. Parameters

To evaluate the mechanism of C_2H_2 dissociation by the MW plasma, the concentration of main products should be correlated with plasma parameters such as flow rate (F) in the discharge tube, discharge power input (W), and the MW cavity position. In this section we consider the normalized concentrations of the main ionic $[F(\Sigma I_{ion})]$ and neutral $[F(\Sigma I_{neutral})]$ species in the plasma at different parameters. The peak intensity of Li^+ is not included in the summation (ΣI_{ion}).

1. MW cavity positions along the stream

The effect of distance from the MW cavity position was investigated. The normalized intensities of ionic and neutral species are shown in Fig. 3 (ionic) and Fig. 4 (neutral). Position A is where the C_2H_2 enters the flow tube. The products undergo reactions between the formation and time of sampling. Sampling at positions $A-D$ allows evaluation of the reaction mechanisms in order of their occurrence.

The total intensity of the ionic species (ΣI_{ion}) increases almost linearly along the flow tube from position A to B to C to D (Fig. 3). However, the normalized concentrations of almost all species hardly change (within a factor of 2) from A to D. Among the listed species the normalized peak intensity

of $C_6H_6^+$ was highest and that of $C_4H_4^+$ was lowest over the entire range.

Among the neutral species (Fig. 4), the normalized concentration of most higher-mass species, including the free radical species C_4H_3, increases, but C_2H_3 and C_2H_5 decrease sharply with increasing distance. These observations indicate that the reduction of C_2H_3 and C_2H_5 takes place by the formation of other polymerized HC species and are consistent with the possibility that the radical species are more reactive than other species.

The C_2H_2 concentration is at minimum at position B, suggesting that conversion reaction and formation take place along the stream, but the high concentration of C_6H_4 is nearly the same over the entire range. The total intensity of neutral species (not shown) is almost constant from A to D. The normalized peak intensity changes with the cavity position in a very complicated way from sample to sample. These behaviors are very different from those of the ionic species.

2. Flow rate dependence

Since position C is most favorable for the observation of total neutral radicals with high normalized concentrations, results are presented for position C only. Figure 5 shows the normalized concentrations of ionic and neutral species in the plasma with increasing flow rate in the plasma tube. The general trend in the $F(\Sigma I)$ values shows that higher-mass species, both ionic and neutral, tend to form at higher pressures. This suggests a chain-polymerization sequence for the polymer species.

Figure 5(a) shows that the peak intensity of $C_2H_2^+$ decreases with increasing flow rate (pressure) in the flow tube, suggesting that these ions are more reactive than other spe-

TABLE I. Normalized mass spectra (see footnote a) of an acetylene plasma with MW power at 30 W and C_2H_2 flow rate at 4 mL/min (plasma pressure 840 Pa). The percentage of intensities of the peaks are relative to the highest peak ($C_6H_4^+$).

	Ionic species				Neutral species		
	This study		Ref. [9]		This study		Refs. [6, 7]
m/z	Formula	(%)[a]	Formula	(%)[b]	Formula	(%)[a]	Formula[c]
17					OH	28	
18					H_2O	230	
26	$C_2H_2^+$	16.6	$C_2H_2^+$	100	C_2H_2	18.5	C_2H_2
27					C_2H_3	159	C_2H_3
28					C_2H_4	10.2	
29					C_2H_5	20.4	
30					$C_2H_6, NO(\Sigma)$	41.5	
36					$(H_2O)_2$	102	
38					C_3H_2	5.7	
39	$C_3H_3^+$	4.0	$C_3H_3^+$	0.8			
41					C_3H_5	12.9	
43					C_3H_7	2.8	
48					C_4	17.4	
50	$C_4H_2^+$	24	$C_4H_2^+$	29	C_4H_2	23.1	C_4H_2
51	$C_4H_3^+$	27	$C_4H_3^+$	6.0	C_4H_3	55.2	C_4H_3
52	$C_4H_4^+$	10	$C_4H_4^+$	1.0	C_4H_4	13.5	C_4H_4
53					C_4H_5	10.1	
54					$C_4H_6, (H_2O)_3$	15.6	
55					C_4H_7	5.2	
56					C_4H_8	9.1	
57					C_4H_9	6.6	
72					C_6	5.4	
74	$C_6H_2^+$	26	$C_6H_2^+$	3.8	C_6H_2	21.1	C_6H_2
75	$C_6H_3^+$	7.5	$C_6H_3^+$	1.5	C_6H_3	29.4	
76	$C_6H_4^+$	100	$C_6H_4^+$	1.5	C_6H_4	39.8	
77	$C_6H_5^+$	23	$C_6H_5^+$	0.4	C_6H_5	8.9	
78	$C_6H_6^+$	5.0			C_6H_6	25.1	
96					C_8	12.9	
98	$C_8H_2^+$	18			C_8H_2	25.3	C_8H_2
100	$C_8H_4^+$	45			C_8H_4	23.4	
101	$C_8H_5^+$	13					
102	$C_8H_6^+$	13			C_8H_6	19.7	
103	$C_8H_7^+$	6.4					
122	$C_{10}H_2^+$	7.9			$C_{10}H_2$	15.3	
124	$C_{10}H_4^+$	33			$C_{10}H_4$	12.1	
126	$C_{10}H_6^+$	38			$C_{10}H_6$	16.0	
128	$C_{10}H_8^+$	5.8					
148	$C_{12}H_4^+$	21					
150	$C_{12}H_6^+$	44					
152	$C_{12}H_8^+$	7.5					
172	$C_{14}H_4^+$	15					
174	$C_{14}H_6^+$	19					
175	$C_{14}H_7^+$	9.0					
176	$C_{14}H_8^+$	11					
196	$C_{16}H_4^+$	8.4					
198	$C_{16}H_6^+$	15					
200	$C_{16}H_8^+$	7.7					

[a]The relative intensities of both the ionic species and of the Li^+ adducts of the neutral species are given as percentages of the height of the highest peak in the mass spectrum of Fig. 2(a), that for $C_6H_4^+$.
[b]Percentage of ion abundance found in 13.3-Pa acetylene discharge, sampled axially. C_2H (1.7%) and C_3H^+ (0.8%) are not listed in this table.
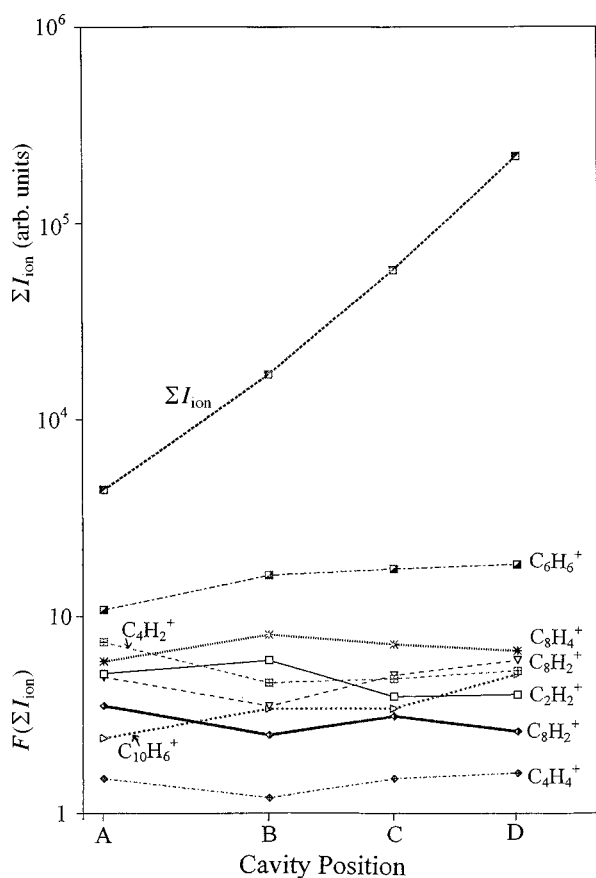[c]C_nH ($n=2,4,6$) species are not listed in this table.

FIG. 3. Total mass spectrometric intensity (ΣI_{ion}) of ionic species and ion distribution [$F(\Sigma I_{\text{ion}})$] at four MW cavity positions. Power input, 30 W; flow rate, 4 mL/min.

FIG. 4. Normalized intensity [$F(\Sigma I_{\text{neutral}})$] of Li$^+$ adduct species at different MW cavity positions. Conditions are as in Fig. 3.

cies, whose concentrations increase. C$_4$H$_2$$^+$ and C$_6$H$_2$$^+$ pass through maximum (around 3 mL/min) $F(\Sigma I_{\text{ion}})$ concentrations as the pressure increases, which indicates that these are being formed as well as converting (reacting). C$_6$H$_4$$^+$, C$_8H_2$$^+$, C$_8H_4$$^+$, and C$_{10}H_6$$^+$ increase gradually with increasing flow rate. In contrast, C$_4$H$_4$$^+$ shows a fairly constant fractional intensity of the ionic species ΣI_{ion}.

Figure 5(b) shows results for the neutral species. At a flow rate of 1 mL/min, any neutral fluxes became so weak that measurements could not be made. HC radicals C$_2$H$_3$ and C$_2$H$_5$ vary significantly over the range, but C$_4$H$_3$ does not. The fractional intensity of the neutral species $F(\Sigma I_{\text{neutral}})$ of C$_2$H$_2$ decreased by a factor of 40 over the range 2–16 mL/min, whereas C$_6$, C$_6$H$_4$, and C$_8$H$_2$ increase by a factor of more than 10. This indicates that the conversion of C$_2$H$_2$ proceeds more efficiently with increasing flow rate (pressure). C$_2$H$_3$, C$_2$H$_5$, and C$_4$H$_2$ pass through maximum (around 4 mL/min) $F(\Sigma I_{\text{neutral}})$ concentrations as the flow rate increases, indicating that these are being formed as well as converting (reacting).

3. MW power dependence

Figure 6 shows the behavior of the total and individual peak intensities of the ionic and neutral products as a function of MW power (in the range 30–120 W). As expected, power affects production in a complex way.

The total peak intensity of the ionic species was hardly changed with increasing MW power, whereas that of the
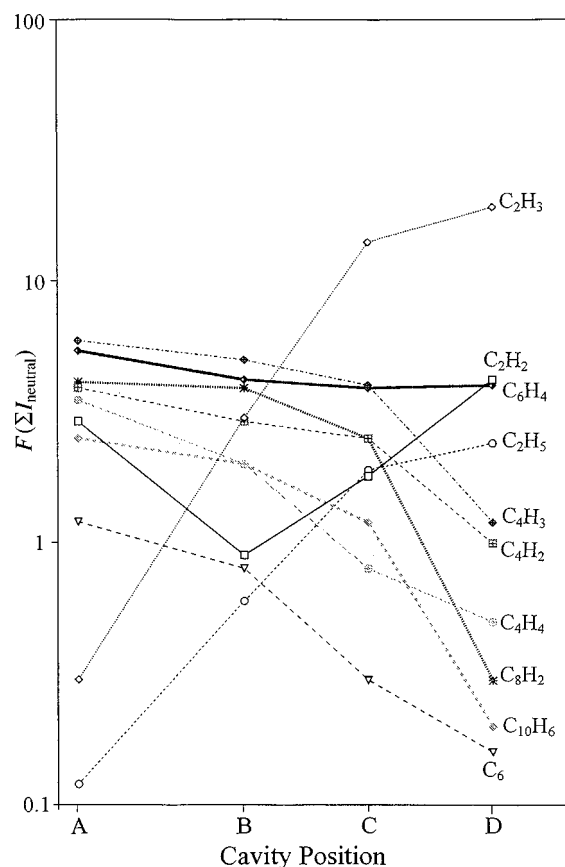
neutral species was highest at 60 W. Increasing the power does not necessarily increase the formation of ions.

Figure 6(a) shows that the peak intensities of C$_6$H$_4$$^+$, C$_8H_2$$^+$, C$_8H_4$$^+$, and C$_{10}H_6$$^+$ were reduced with increasing MW power, while those of other species were either increased or almost constant. This suggests that dissociation reactions of the higher polymer products are most likely to be observed at high discharge powers.

Figure 6(b) shows that neutral radical production increased at 60 W and disappeared at 120 W, leaving almost exclusively the closed-shell neutral species. However, for most of the closed-shell neutral products, there still exists an optimal power input for the highest formation rate. At powers higher than the optimal, more recombinations of radicals may occur in the plasma.

4. Relationship between ionic and neutral species

It is well known that the reaction chain in the plasma is initiated by the ionization of C$_2$H$_2$ by a free electron 3–40 eV in energy in a MW discharge plasma [23]. The primary ions transfer their charge to molecules or radicals. This forms reactive ions that are responsible for the subsequent chemical reactions that create the various neutral radicals in the MW plasma.

Any reaction scheme used to interpret data must necessarily take into account that almost all the significant neutral species coexist with the corresponding ionic species in the C$_2$H$_2$ discharge, with the exception that we detected C$_3$H$_3$, C$_6$, C$_4$, and C$_8$, but not the corresponding ions. Because ions
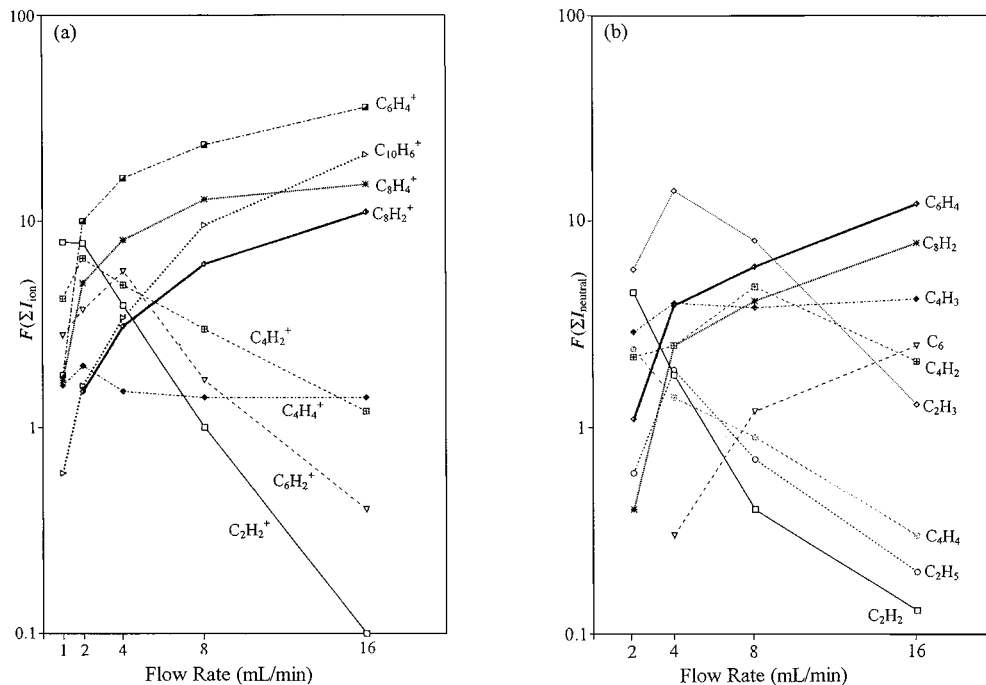
FIG. 5. Normalized intensity of (a) ionic and (b) neutral species as a function of flow rate (pressure) in the range 1–16 mL/min (and a consequent pressure of 213–2133 Pa) at MW cavity position C, at 30-W power input.

and their corresponding neutral species do not necessarily behave similarly, elaboration on the mechanism will not be easy. Ions of the form $C_nH_m^+$ ($n>m$) cannot be easily generated by the ionic condensation of acetylene plasma. The presence of corresponding neutrals is therefore relevant to the neutral chemistry that proceeds in the discharge. The lack of neutral and ionic species with odd-numbered carbons means that cleavage of the acetylene molecule to CH radicals does not take place to any significant extent.

C. Reaction schemes

This section discusses reactions of various types, such as ion-molecule and radical-molecule reactions, to allow our results to be satisfactorily modeled. A gas discharge can be looked at as a composite of many of the processes existing in the shock-tube pyrolysis, photolysis, and chemical ionization studies cited earlier. Those studies prove to be helpful in explaining our results.
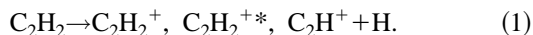

FIG. 6. Peak intensity of several (a) ionic and (b) neutral species as a function of MW power at a flow rate of 4 mL/min at MW cavity position C. The total intensities of ionic and neutral species are also given.
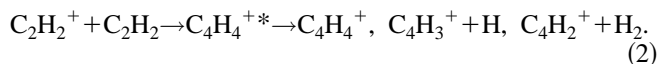
1. Ionic processes

The ion-molecule reaction chemistry plays an important role. The primary ion production in the C$_2$H$_2$ MW plasma is given by
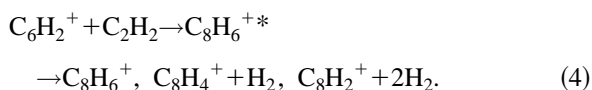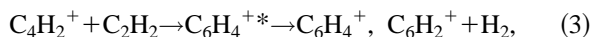
$$C_2H_2 \rightarrow C_2H_2^+, \ C_2H_2^{+*}, \ C_2H^+ + H. \tag{1}$$

As no significant amount of C$_2$H$^+$ is observed under any plasma conditions, our discussion will concern only C$_2$H$_2^+$.

It can be safely assumed from the abundance of C$_4$H$_4^+$, C$_4$H$_2^+$, and C$_4$H$_3^+$ that condensation reactions proceed through an excited intermediate C$_4$H$_4^{+*}$: Depending on the pressure, this decomposes to the principal secondary ions C$_4$H$_2^+$ and C$_4$H$_3^+$:

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_4^{+*} \rightarrow C_4H_4^+, \ C_4H_3^+ + H, \ C_4H_2^+ + H_2. \tag{2}$$
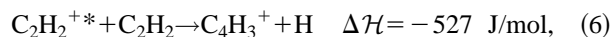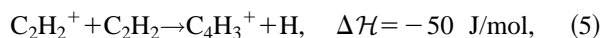
With the formation of C$_n$H$_2^+$ ($n = 4, 6, 8, 10$), the polymerization process in the MW plasma will most likely continue by continuous reaction with C$_2$H$_2$. As seen in Fig. 5(a), the flux of C$_2$H$_2^+$ decreases as that of C$_4$H$_2^+$ increases and then the flux of C$_4$H$_2^+$ decreases as that of C$_6$H$_2^+$ increases.

By the same token, possible steps to the formation of highly unsaturated C$_n$H$_4^+$ ($n = 4, 6, 8, 10, 12, 14, 16$) and C$_nH_6^+$ ($n = 6, 8, 10, 12, 14, 16$) ionic series are

$$C_4H_2^+ + C_2H_2 \rightarrow C_6H_4^{+*} \rightarrow C_6H_4^+, \ C_6H_2^+ + H_2, \tag{3}$$

$$C_6H_2^+ + C_2H_2 \rightarrow C_8H_6^{+*}$$
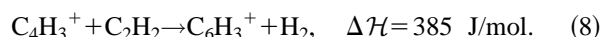$$\rightarrow C_8H_6^+, \ C_8H_4^+ + H_2, \ C_8H_2^+ + 2H_2. \tag{4}$$

Reactions (3) and (4) are known to be among the most probable reaction paths available for condensation reactions of C$_2$H$_2^+$ with C$_2$H$_2$ [24]. The absence of C$_6$H$_3^+$ or C$_8$H$_3^+$ indicates the collisional stabilization of C$_6$H$_4^+$ or C$_8$H$_4^+$ in the plasma, which in turn would eliminate a source of these dissociated ions.

The formation of the C$_4$H$_3^+$ ion by the following exothermic reactions is well known from mass spectrometry [24]:

$$C_2H_2^+ + C_2H_2 \rightarrow C_4H_3^+ + H, \quad \Delta\mathcal{H} = -50 \ \text{J/mol}, \tag{5}$$

$$C_2H_2^{+*} + C_2H_2 \rightarrow C_4H_3^+ + H \quad \Delta\mathcal{H} = -527 \ \text{J/mol}, \tag{6}$$

The presence of C$_3$H$_3^+$ and C$_6$H$_3^+$ indicates collisions that were more energetic than thermal. These ions may be formed in

$$C_2H_2^+ + C_2H_2 \rightarrow C_3H_3^+ + CH, \quad \Delta\mathcal{H} = 109 \ \text{J/mol}, \tag{7}$$

$$C_4H_3^+ + C_2H_2 \rightarrow C_6H_3^+ + H_2, \quad \Delta\mathcal{H} = 385 \ \text{J/mol}. \tag{8}$$
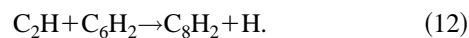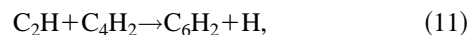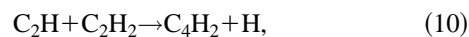
2. Neutral species processes

The following reaction of decomposition of C$_2$H$_2$ by kinetic electrons in the MW plasma is feasible [14]:

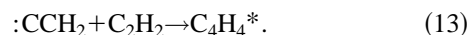$$C_2H_2 \rightarrow C_2H + H. \tag{9}$$

C$_2$H, which is a major species in the photolytic decomposition of C$_2$H$_2$, may be the chain-reaction carrier for the general sequence given in Eqs. (10)–(12) and suggested by Kiefer and Von Drasek [25] for acetylene pyrolysis:

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H, \tag{10}$$

$$C_2H + C_4H_2 \rightarrow C_6H_2 + H, \tag{11}$$

$$C_2H + C_6H_2 \rightarrow C_8H_2 + H. \tag{12}$$

Duran, Amorebieta, and Colussi [26] proposed the importance of singlet vinylidene (:CCH$_2$) and its role in the C$_2$H$_2$ mechanism. The first step involves isomerization of acetylene to vinylidene followed by insertion of vinylidene into the C—H bond of C$_2$H$_2$, forming excited vinylacetylene C$_4$H$_4^*$ [Eq. (13)]. This suggestion is supported indirectly by our observation of abundant C$_4$H$_4$ species,

$$:CCH_2 + C_2H_2 \rightarrow C_4H_4^*. \tag{13}$$

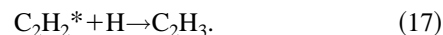C$_4$H$_4^*$ may convert by several different paths [Eqs. (14)–(16)], which provides an explanation for many of the products found in this study, such as C$_4$, C$_6$, and C$_8$:

$$C_4H_4^* \rightarrow C_4H_4, \ C_4H_2 + H_2, \ C_4 + 2H_2, \tag{14}$$

$$C_4H_4^* + C_2H_2 \rightarrow C_6H_6^*, \tag{15}$$

$$C_6H_6^* \rightarrow C_6H_6, \ C_6H_4 + H_2, \ C_6H_2 + 2H_2, \ C_6 + 3H_2. \tag{16}$$

The increasing fractional concentration of C$_6$ with pressure [Fig. 5(b)] is accompanied by a decrease in C$_4$H$_4$, which is an assumed precursor. This behavior is consistent with the results of pressure dependence.

From our results, one would expect a much radical chemistry in the C$_2$H$_2$ discharge. A vinyl radical C$_2$H$_3$ was directly observed as a major product. In addition to reaction (10)–(13), the other possible reaction for polymerization starts with this species. The drop in the fractional intensity of the neutral species $F(\Sigma I_\text{neutral})$ C$_2$H$_2$ from D to C in the plasma tube and the increase in that of C$_2$H$_3$ implies the reaction in Eq. (17), in which a hydrogen atom is a counterpart for C$_2$H$_3$ formation. It is well known that electrons present in the plasma should produce hot hydrogen atoms [25]

$$C_2H_2^* + H \rightarrow C_2H_3. \tag{17}$$

If C$_2$H$_3$ is supplied, then the interaction between C$_2$H$_3$ and C$_2$H$_2$ or other HC molecules is highly probable; the free radical interaction with C$_2$H$_2$ and other HC molecules is highly exothermic, indicating the production of the larger HC species. Reactions among radical-involved condensations leading to polymeric products may well dominate the chemistry of the acetylene discharge.

As shown in Table I, neutral species of the form C$_m$H$_n$ ($n > m$), but not the corresponding ions, are formed in the acetylene plasma. The presence of the neutral species is therefore relevant to the neutral chemistry that proceeds in the plasma discharge. A possible reaction to yield these species is given by

$$C_mH_m + H \rightarrow C_mH_{m+1}. \tag{18}$$
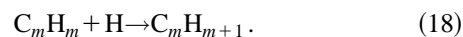
C_mH_n neutral species may react with the available hydrogen atoms.

IV. CONCLUDING REMARKS

The mass spectrometer Li^+ reactor setup was successfully used for the simultaneous analysis of neutral and ionic species in the C_2H_2 system and allowed general criteria for the effects of the process parameters to be derived. It can be concluded that a pure C_2H_2 MW discharge results in a high conversion of C_2H_2 to ionic and neutral polymer products. This process is explained by two types of general reactions: the interaction between free radicals and HC molecules and the interaction between ion radicals and HC molecules. The observed ion chemistry is very much like that found by high-pressure mass spectrometry: ionic species with even-numbered carbon atoms dominate. Almost all the significant neutral species coexist with the corresponding ionic species, except for C_4^+, C_6^+, C_8^+, and $C_mH_n^+$ ($n>m$). An interac-tion between a hydrogen atom and HC molecules is the mechanism for the C_mH_n ($n>m$) species.

Although the experimental system described here is not necessarily the same as that in a microwave-plasma-enhanced chemical-vapor-deposition system, only in this study has a diagnosis been made to determine intermediary free radical and potential reaction schemes. Simultaneous measurements of ionic and neutral species by mass spectroscopy have been shown to be useful in verifying the plasma characteristics.

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