

## Identification of intermediate radicals in the $\text{CH}_4$ microwave plasma by the $\text{Li}^+$ attachment method

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We (i) describe the complete  $\text{Li}^+$ -adduct mass spectrum of the  $\text{CH}_4$  microwave discharge plasma, obtained by ion attachment techniques, (ii) give evidence that many radicals are produced in the plasma, and (iii) present a preliminary spectral identification analysis. The identified species are  $\text{C}_n\text{H}_{2n-1}$  ( $n=2-13$ ),  $\text{C}_n\text{H}_{2n+1}$  ( $n=2-13$ ),  $\text{C}_n\text{H}_n$  ( $n=2,4,5,6$ ), and so on.

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In order to demonstrate that a recent development of the  $\text{Li}^+$  ion attachment and quadrupole mass spectrometer technique for the sensitive detection of intermediate radicals will yield important data for various radical reactions, we have investigated the identification of the principal radical species produced by the  $\text{CH}_4$  microwave (MW) discharge. We have succeeded in detecting various kinds of hydrocarbon polymer radicals, which were  $\text{C}_n\text{H}_{2n-1}$  ( $n=2-13$ ),  $\text{C}_n\text{H}_{2n+1}$  ( $n=2-13$ ),  $\text{C}_n\text{H}_n$  ( $n=2,4,5,6$ ), and so on. The concurrent formation of these types of radicals is experimental evidence on radical involvement in plasma-induced polymerization and may be characteristic of plasma, suggesting the importance of radical-molecule reactions in the plasma environment.

Intermediate radicals have short lifetimes. Furthermore, their steady-state concentration in a reacting gas phase is sometimes low. The combination of small concentrations and short lifetimes has offered a real challenge to scientists [1].

On the other hand, it has been widely recognized that neutral radical species are responsible for the plasma treatment [2-4], such as the deposition of hydrogenated

amorphous carbon thin films as well as crystal diamond films, the etching of highly integrated circuits, and surface graft polymerization. However, the difficulties of radical detection have hampered the development of insights into the process mechanisms.

We believe that the present study concerns one of the most important problems that had to be resolved before the radical contribution to the total reaction schemes could be determined in plasma chemistry.

The apparatus is shown in Fig. 1. A Shimadzu atmospheric pressure ionization quadrupole mass spectrometer with a  $\text{Li}^+$  ion attachment reaction chamber (RC) was used [5,6]. A stream of reaction products from a quartz discharge flow tube is directed into the alkali-metal ion attachment reaction chamber.

The RC has a glass bead ( $\text{Li}^+$  emitter) which contains the alkali-metal oxide (lithium oxide in the present study) in an aluminosilicate matrix. By heating this bead, lithium ions are produced [7]. These parent ions, in turn, ionize the radical products ( $R$ ) by adduct formation  $(R+\text{Li})^+$ .  $(R+\text{Li})^+$  complexes are formed by termolecular association reactions [8,9]. Parent-daughter ion

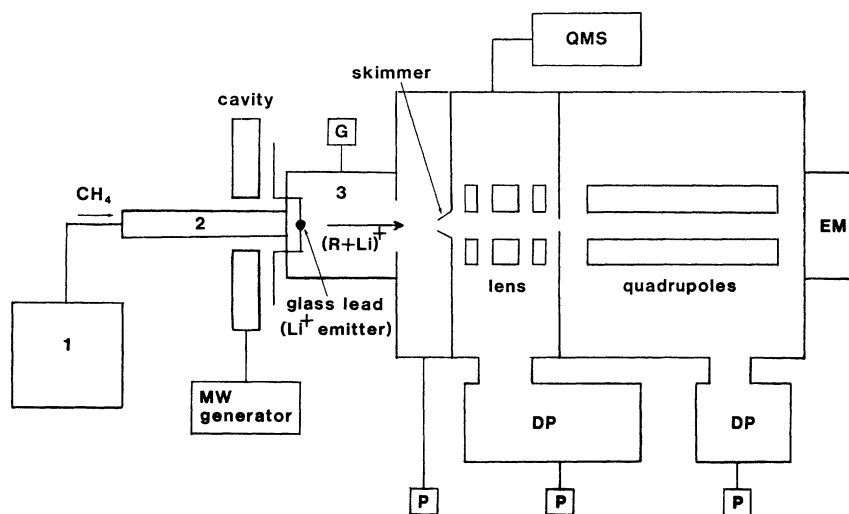


FIG. 1. Schematic of experimental setup. (1) Gas inlet system with flowmeter; (2) quartz discharge flow tube; (3) reaction chamber (RC); pressure gauge (G); rotary pumps (P); diffusion pumps (DP); detection unit with electron multiplier (EM); electron ionization quadrupole mass spectrometer (QMS) for gas analysis.

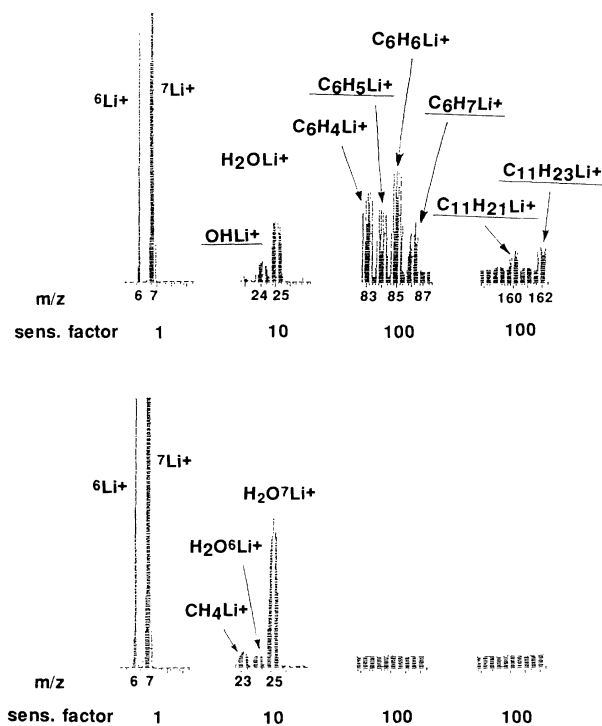


FIG. 2. Partial mass spectra of  $\text{Li}^+$  ion adducts. The upper stage shows the discharge-ion conditions and the lower stage the discharge-off conditions. The underlined peaks indicate the radicals observed. The intensities of  $\text{Li}^+$  (parent ion) exceed the scale of the representation, which is chosen for the purpose of demonstrating daughter ion peaks due to radicals.

pairs  $[\text{Li}^+ / (\text{R} + \text{Li})^+]$  are measured to detect the intermediate radicals and to assign their possible source.

The discharge flow system includes a Beenakker-type cavity, MW power generator with an operating frequency of 2.45 GHz, a quartz discharge flow tube, and flow lines. The discharge tube was built from 4-mm-i.d. quartz and was approximately 120 cm long. The quartz tube ends in

the RC about 10 mm in front of the  $\text{Li}^+$  emitter. The experimental conditions employed were as follows: The RC pressure was 0.22 Torr with a methane gas fed at a flow rate of 22 ml/min and the MW input power was 6 W.

Figure 2 shows the practical mass spectra over regions  $m/Z$  5–9, 23–27, 83–87, and 158–162. These  $\text{Li}^+$ -adduct data taken with the discharge on (upper trace) have additional peaks in the spectrum, compared with the data taken with the discharge off (lower trace). Thus the additional peaks in the upper stage are attributed to ion attachment to chemical species effusing from the plasma. All measurements were made under conditions in which the system was at steady-state conditions.

The presence of hydrocarbon polymer radicals is denoted by an increase in the current of the  $\text{Li}^+$ -adduct ions. For example, the peak  $m/Z$  160 and 162, due to the  $\text{Li}^+$ -adduct ions, are assigned to those of  $\text{C}_{11}\text{H}_{21}$  and  $\text{C}_{11}\text{H}_{23}$  radicals, respectively. Also present in this spectrum is the production of the OH radical which was detected very clearly as  $\text{OHLi}^+$  ions. This radical may be anticipated as a result of the discharge reaction of  $\text{H}_2\text{O}$  contained in the  $\text{CH}_4$  discharge gas as impurities.

Table I shows the mass spectral data taken under the same experimental conditions as measured in Fig. 2. The  $\text{C}_n\text{H}_{2n-1}$  and  $\text{C}_n\text{H}_{2n+1}$  radicals, where  $n = 2-13$ , have been detected. The intensity trend is clear; species with the higher  $n$  number decrease in intensity.  $\text{C}_n\text{H}_n$  with carbon number  $n$  up to 6 was also produced. However, no CH radical was observed. Besides that, other hydrocarbon species [see footnote a of Table I] such as  $\text{C}_4\text{H}_5$ ,  $\text{C}_5\text{H}_7$ ,  $\text{C}_6\text{H}_5$ , and  $\text{C}_6\text{H}_7$  were produced in the plasma. But some peaks are not included in Table I. Most of them are probably oxygen-containing species, such as OH,  $\text{C}_2\text{H}_4\text{O}$ ,  $\text{C}_2\text{H}_5\text{O}$ ,  $\text{C}_3\text{H}_6\text{O}$ , and  $\text{C}_3\text{H}_7\text{O}$ . These species may be due to the presence of  $\text{O}_2$  and  $\text{H}_2\text{O}$  in methane or in the gas flow system as impurities. It should be noted, however, that some peaks have an uncertain identity since their validity is only based on the mass number.

The preliminary experiments showed that adding hydrogen to the  $\text{CH}_4$  gas resulted in a significant effect on the major product distribution. All the radical peaks ob-

TABLE I. Analysis of radical products formed from the MW discharge plasma of pure  $\text{CH}_4$  in terms of mass identification and classification in their formula.

Type	Chemical species
$\text{C}_n\text{H}_{2n-1}$	$\text{C}_2\text{H}_3(100)^a$ , $\text{C}_3\text{H}_5(98)$ , $\text{C}_4\text{H}_7(90)$ , $\text{C}_5\text{H}_9(22)$ , $\text{C}_6\text{H}_{11}(18)$ , $\text{C}_7\text{H}_{13}(15)$ , $\text{C}_8\text{H}_{15}(13)$ , $\text{C}_9\text{H}_{17}(7)$ , $\text{C}_{10}\text{H}_{19}(6)$ , $\text{C}_{11}\text{H}_{21}(4)$ , $\text{C}_{12}\text{H}_{23}(3)$ , $\text{C}_{13}\text{H}_{25}(2)$
$\text{C}_n\text{H}_{2n+1}$	$\text{C}_2\text{H}_5(68)$ , $\text{C}_3\text{H}_7(61)$ , $\text{C}_5\text{H}_9(46)$ , $\text{C}_5\text{H}_{11}(41)$ , $\text{C}_6\text{H}_{13}(34)$ , $\text{C}_7\text{H}_{15}(24)$ , $\text{C}_8\text{H}_{17}(17)$ , $\text{C}_9\text{H}_{19}(10)$ , $\text{C}_{10}\text{H}_{21}(10)$ , $\text{C}_{11}\text{H}_{23}(5)$ , $\text{C}_{12}\text{H}_{25}(4)$ , $\text{C}_{13}\text{H}_{27}(1)$
$\text{C}_n\text{H}_n$	$\text{C}_2\text{H}_2^b(20)$ , $\text{C}_4\text{H}_4^b(4)$ , $\text{C}_5\text{H}_5(40)$ , $\text{C}_6\text{H}_6^b(35)$
Others <sup>c</sup>	$\text{C}_4\text{H}_3(61)$ , $\text{C}_4\text{H}_5(49)$ , $\text{C}_5\text{H}_7(30)$ , $\text{C}_6\text{H}_4^b(28)$ , $\text{C}_6\text{H}_5(24)$ , $\text{C}_6\text{H}_7(20)$

<sup>a</sup>The relative intensities of the  $m/Z$  peaks representing percent values are given.

<sup>b</sup>Those molecules may have high enough  $\text{Li}^+$  affinities to be attached by  $\text{Li}^+$  ions.

<sup>c</sup>There are possibilities [12] that these species are produced through the elimination of  $\text{H}_2$  upon ionization by  $\text{Li}^+$  attachment. For example,  $\text{C}_4\text{H}_7\text{Li}^+ \rightarrow \text{C}_4\text{H}_5\text{Li}^+ + \text{H}_2$ .

served in the pure  $\text{CH}_4$  gas were almost completely depressed. We temporarily assume that the excited states will ionize the radicals by collisions. A more detailed report is planned to be presented elsewhere.

In conclusion, the recently developed ion attachment technique incorporated with quadrupole mass spectrometry has been successfully used for the direct identification of the hydrocarbon radicals in the MW plasma of  $\text{CH}_4$ . The conclusion can be summarized as follows: (i) The formation of various kinds of polymer radicals (up to  $\text{C}_{13}$ ) was confirmed experimentally and may be characteristic of plasma in general; (ii) the formations of the polymer hydrocarbon radicals can be achieved with a simple apparatus; and (iii) the present results not only contribute to enhancing our understanding

of the chemical component of the plasma, but also provide fresh evidence that the radical-molecule reactions are involved in the polymerization process of the  $\text{CH}_4$  plasma [10].

By providing a means of detecting intermediate radicals in gaseous systems, the present method can be of immediate help in the study of combustion processes, chemical vapor deposition plasma treatment processes, and atmospheric reactions, in which OH and  $\text{O}_2\text{H}$  figure prominently as an intermediate product [11]. It should also be noted that there are a number of ways in which the ion attachment technique for the radical detection can be improved at little cost in complexity, chiefly by substituting  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Al}^+$ ,  $\text{Ag}^+$ ,  $\text{Ga}^+$ , and  $\text{Fe}^+$  for the present  $\text{Li}^+$  species.

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