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Mass spectroscopic study of CH_3 radicals produced in a hollow cathode discharge cell

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Neutral CH_3 radicals in a hollow cathode discharge cell containing methane have been detected with a quadrupole mass spectrometer, using the threshold ionization technique. With the experimental conditions employed in this work the measured efficiency in CH_3 production has been 0.2%, which is higher than that shown for other types of discharges in the bibliography. On the other hand a high depletion of the CH_4 density has been observed and the mass spectrum of the discharge shows the appearance of compounds at $m = 25$, 26, and 27, proceeding from recombination processes.

I. INTRODUCTION

The methyl radical is one of the most important molecular free radicals in chemical reactions. It may be one of the most abundant free radicals in the interstellar medium, as shown by calculations of the molecular evolution of dark clouds.¹ It has been identified as the most dominant deposition species in methane rf glow-discharge plasmas used for depositing amorphous and diamond-like films² and it plays an important role during the initial stages of hydrocarbon combustion and in atmospheric chemistry. So, production of CH_3 in the laboratory is nowadays of great interest in order to characterize it spectroscopically for its atmospheric and interstellar space observation^{3,4} and also to obtain thin films with better efficiency and accuracy.²

Being chemically unstable, CH_3 has been produced from various compounds in the laboratory, mainly by UV laser photolysis,⁵ pyrolysis,⁶ and glow discharge,^{7,8} for optical spectroscopic studies and by rf excitation and glow discharges^{2,9,10} for deposition work. But so far, to our knowledge, CH_3 has not been produced in a hollow cathode discharge cell, although its electrical characteristics are well known and similar to those of glow discharges, its behavior may clarify the carbon deposition processes on metal chambers employed for fusion and plasma studies and moreover it is recognized to be a very good source for spectroscopic studies.

In fact, hollow cathode discharges can be produced with dc, ac, or pulsed current, which enables the use of different kinds of detection schemes; they are stable over a large range of currents and pressures, they can be used to measure substances very difficult to evaporate, and thanks to the low temperature of the gases involved in this type of discharge, with adequate refrigeration of the cathode, spectra can be obtained with better resolution (Doppler limited) than in other sources. With some new designs^{11,12} these discharges can present a long optical path for absorption spectroscopy in a multipass cell (White cell configuration¹³). At the same time they allow the use of the very sensitive optogalvanic detection method. On the other hand designs with a smaller cathode are useful for emission

studies¹⁴ and are expected to be very adequate for the new techniques of stimulated Raman spectroscopy.

To prove CH_3 formation in a hollow cathode discharge cell, a quadrupole mass spectrometer can be used as a way of measuring the absolute efficiency of radical formation in the discharge, if a threshold ionization technique is introduced in order to eliminate abundant formation of fragment CH_3^+ ions from the parent gas CH_4 . The threshold ionization technique is based on the difference between the appearance potential of dissociative ionization of CH_4 to give CH_3^+ and the ionization potential of the free radical ($\text{CH}_3 \rightarrow \text{CH}_3^+$).^{9,10}

In this work a hollow cathode discharge cell has been built and used for the first time to produce methyl radicals from CH_4 discharges and its absolute density has been measured by the threshold mass spectrometric method, proving a good efficiency in CH_3 production. A very significant depletion of the parent molecule CH_4 with the electric power of the discharge has been observed, and looking for the mechanism of the formation and destruction of transient species and heavy compound deposition, the mass spectra of the discharge has been obtained up to 360 amu.

II. EXPERIMENTAL SETUP

The apparatus used in this work is shown schematically in Fig. 1. For CH_3 detection a quadrupole mass spectrometer Extrel (mass analyzer 7-324-9, power and high Q -head 011-15), with a secondary electron multiplier (SEM) in the current mode as detector and a Keithley 614 electrometer were employed, varying electron impact energy and using the threshold mass spectrometric technique. This quadrupole was used also to obtain the mass spectrum of the discharge up to 360 amu with the aid of a digital Tecktronix 2430 A oscilloscope in the average mode. A second quadrupole mass spectrometer Balzers QMG 112 with a Faraday cup was used as a partial pressure detector for studies of CH_4 depletion with electrical power and for normalization purposes. The chamber with the two mass spectrometers was backed up by means of a $35 \text{ m}^3/\text{h}$ rotary

FIG. 1. Schematic diagram of the experimental setup.

pump, a 300 ℓ /s oil pump, and a liquid nitrogen trap. A vacuum of 7.10^{-5} Pa was achieved before gas input.

The hollow cathode discharge cell was based on the design of Dynamus and Van den Heuvel¹⁵ with a 5-cm-diam, 70-cm-long copper cathode and a stainless-steel anode, both refrigerated by water. The anode has a diameter of 15 mm and is mounted on a side arm at midpoint of the cell. The discharge strikes from the anode through a hole cut in the cathode. Occurrence of the discharge outside the cathode tube was prevented by Teflon seals and a glass tube inserted between the electrodes. Maintenance of the discharge for different ranges of pressure at constant voltage can be controlled by varying the length of this glass tube, which establishes the distance between electrodes; a value of 6 cm maintained the discharge over a wide range of pressures around the values used here. Nevertheless the stability of the discharge is strongly affected by dirtiness of the electrodes and cleaning the solid residues of the discharge in the cell is more frequently necessary when working at the highest values of CH_4 pressure or electrical power. A 1200 W audio amplifier fed by a sine wave generator drove a step-up transformer to produce a 3 kV, 1200 Hz voltage which was applied to the anode of the cell through a 1500 Ω ballast resistor. The cell acts as a rectifier and passes current only on those half-cycles for which the anode is positive. Since the CH_3 radical is known to have a relatively long lifetime, above 1 ms for relatively small pressures of CH_4 ,^{9,16} a significative modulation in CH_3 density was not expected at this frequency of excitation.

Communication between the discharge cell and the quadrupoles' chamber was established by a gate valve and an aperture with a diameter of 180 μm , inserted just in the center of one of the cathode ends with the aid of a distance adjustable Teflon support. A flow of about 5×10^{-5} mol s^{-1} of research grade CH_4 through the cell was maintained by a 18 m^3/h rotary pump and a liquid-nitrogen trap inserted in the pumping line. With a mean pressure in the discharge cell of 20 Pa a total pressure about 2×10^{-4} Pa in the quadrupole chamber was obtained.

III. RESULTS

In Fig. 2 the depletion of CH_4 concentration with electric power of the discharge at a constant pressure of 25 Pa

FIG. 2. Depletion of CH_4 density with the electric power of the discharge. $P = 25$ Pa.

and a residence time of 5 s is shown, as detected with the Faraday cup of the Balzers mass spectrometer. It was monitored at 15 amu of the CH_4 fragmentation pattern with an electron ionization energy of 100 eV. These measurements were taken about half an hour after the discharge was established because a rapid decrease in CH_4 density at constant power was observed during the first minutes, until it was fully stabilized. In fact the initial density of CH_4 before discharge setting was four times larger than the one corresponding to the maximum value given in Fig. 2 (0 W). This CH_4 depletion is consistent with the calculated and experimental dissociation rates of Ref. 17 for an equivalent value of flux and electrical power in a rf discharge.

As can be seen in Fig. 2, the CH_4 number density falls with increasing power in an approximately exponential shape. This is in agreement with the result obtained by Davies and Martineau¹⁸ on a deposition reactor, measured with infrared diode laser absorption spectroscopy. Similar results were obtained in the present work for all the masses of the CH_4 fragmentation pattern, as measured from the mass spectra of methane for several power values of the hollow cathode discharge.

A mass spectrum of the discharge up to 360 amu was also obtained to investigate the formation of compounds heavier than 16 amu as a result of recombination between light products. Kline *et al.*² and Rhallabi and Catherine¹⁷ have estimated the most likely homogeneous and heterogeneous reaction paths leading to the deposition of amorphous carbon thin films in methane glow discharge. Toy-

FIG. 3. Quadrupole mass spectrometer CH_3^+ output current as a function of electron beam energy E_e . (a) Open circles: discharge off. Dots: discharge on (800 V, 95 mA, 1.2 KHz, 70 Pa) using a semilogarithmic scale. (b) The same discharge off results (open circles) and Ref. 22 data (continuous line) in a linear scale.

oda *et al.*⁹ and Studniarz and Franklin,¹⁹ detected CH_3^+ and C_2H_5^+ as the most abundant ions and Davies and Martineau¹⁸ have measured a significant concentration of C_2H_4 in a deposition reactor. In our mass spectrum an increase in concentration was not observed for any mass up to 360 amu (with the available sensitivity and background level), except for those of $m/e = 25, 26$, and 27 , belonging to C_2H^+ , C_2H_2^+ , and C_2H_3^+ , for which a significant increase was observed with the discharge on. These products can be thought to be due to the fragmentation pattern of some of the C_2H_x compounds detected in the preceding works.

Figure 3(a) shows a semilogarithmic plot of the output current of the Extrel quadrupole mass spectrometer for CH_3^+ ($m/e = 15$) as a function of electron beam ionization energy. The lower curve (open circles) was obtained without current in the hollow cathode discharge cell, whereas the upper one (dots) was obtained with a discharge of 800 V, 95 mA, at a modulation frequency of 1.2 KHz. Pressure in the cell was maintained at 70 Pa and measured with a Pirani gauge. The electron beam energy of the Extrel ionizer was calibrated by measuring the ionization threshold of argon (15.75 eV).²⁰ The electron energy scale thus obtained is further corroborated by the good concordance between the output current curve as a function of electron energy for the $\text{CH}_4 \rightarrow \text{CH}_3^+$ process (discharge off condition) and the results of Chatham *et al.*²² for the same system, as can be seen in Figs. 3(b) and 4 (in Fig. 4 the output currents of the present experiment have

been normalized to the absolute cross section values determined by the mentioned authors). The spread in the electron energy distribution of our experiment is not exactly known, we have made a rough estimate of its value from the deconvolution of the $\text{Ar} \rightarrow \text{Ar}^+$ signal near threshold. Assuming a gaussian for the approximate shape of the electron energy distribution we get a variance of ~ 0.3 eV.

There is a difference of about 4 eV between the dissociative ionization threshold of $\text{CH}_4 \rightarrow \text{CH}_3^+$ (14.3 eV)⁹ and the CH_3 radical ionization threshold (9.8 eV).²¹ Due to this fact, the signal corresponding to the $\text{CH}_4 \rightarrow \text{CH}_3^+$ process [see Fig. 3(b)] is expected to fall very steeply for values of the electron energy below the threshold for ionization (the remaining signal being caused by spread of the electron energy distribution), thus the observable difference between upper and lower curve in Fig. 3(a) is attributed to electron impact ionization of CH_3 effusing from the plasma when the discharge is on. Other possible sources of the $m/e = 15$ signal are very unlikely under the conditions of the present experiment. As indicated, before no significant increase in the signal of ethane was observed in the monitor detector (run at 90 eV electron energy) when the discharge was on; in any case the threshold for the dissociative ionization of C_2H_6 to give CH_3^+ is very similar to that of CH_4 and the cross section is much smaller than for $\text{CH}_4 \rightarrow \text{CH}_3^+$.²² Excited methane or any other species formed in the discharge are not expected to reach the ionization region of the detector (placed at a distance of ~ 50 cm from the sampling hole) but rather to decay either by

FIG. 4. $\text{CH}_4 \rightarrow \text{CH}_3^+$ quadrupole output signal without discharge (dots) normalized to the absolute cross sections of Ref. 22 (continuous line).

spontaneous emission or by collisional quenching. As can be seen in Fig. 3(a), the contribution of the methyl radical to the total CH_3^+ signal above 15 eV is negligible due to its small concentration as compared with CH_4 although, in agreement with Refs. 22 and 23, the $\text{CH}_3 \rightarrow \text{CH}_3^+$ cross sections are supposedly larger than those for $\text{CH}_4 \rightarrow \text{CH}_3^+$.

Therefore the CH_3 density n in the plasma is proportional to the difference between both quadrupole output currents ΔI below ~ 14 eV and, following Ref. 9, it can be obtained from the equation

$$\Delta I = I(\text{discharge on}) - I(\text{discharge off}) \\ = K\sigma(E_e)n, \quad (1)$$

where $\sigma(E_e)$ represents the CH_3 ionization cross section for each value of electron impact energy and K is a constant which depends on the sensitivity of the quadrupole mass spectrometer, the electron beam current and the efficiency of the CH_3 radical collection across the extracting hole. K can be obtained from the discharge-off CH_3^+ signal due to CH_4 fragmentation if Eq. (1) is applied replacing n by CH_4 density and $\sigma(E_e)$ by the dissociative ionization cross section.

Experimental I (discharge off) values for the $\text{CH}_4 \rightarrow \text{CH}_3^+$ process between 15 and 30 eV are shown in Fig. 4 (dots) and normalized to the absolute cross sections of Chatham *et al.*²² (continuous line), giving a very good agreement between them. Ionization cross sections for $\text{CH}_3 \rightarrow \text{CH}_3^+$ are assumed to be almost the same as those obtained by Baiocchi *et al.* with $\text{CD}_3 \rightarrow \text{CD}_3^+$ ²³ for each electron ionization energy. CH_3 temperature is supposed to be equal to that of CH_4 (~ 300 K).

Using this procedure we have obtained, with the conditions given before, a concentration of CH_3 radicals corresponding to a 0.2% efficiency in CH_3 production from the CH_4 parent gas. This value can be compared with the value of 0.1% obtained by Toyoda *et al.* in a methane rf discharge.⁹ Yamada *et al.*¹⁶ obtained an efficiency of 0.05% from CH_3I , $(\text{CH}_3)_2\text{CO}$ and other compounds by pyrolysis or in a 60 Hz discharge, as measured by diode laser ab-

sorption spectroscopy. Until now, to our knowledge, only UV laser photolysis of CH_3I or CH_3OH with high laser energy (180 mJ/pulse) have been proven to be a more efficient method in peak CH_3 production (1%),²⁴ although the mean efficiency is smaller.

IV. CONCLUSIONS

In this work a hollow cathode of CH_4 discharge cell has been used as a source of CH_3 radicals and a relatively high efficiency in methyl production has been proven. So hollow cathode discharges seem to be useful sources of CH_3 production for spectroscopic and deposition applications.

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