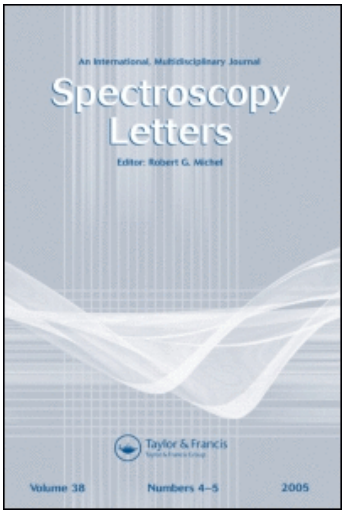

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M. A. Gondal[a]; Zain H. Yamani[b]; A. Dastgeer[a]; M. A. Ali[c]; A. Arfaj[a]
[a] Center for Applied Physical Sciences, Research Institute, King Fahd University of Petroleum and Minerals Dhahran, Dhahran, Saudi Arabia [b] Department of Physics, King Fahd University of Petroleum and Minerals Dhahran, Dhahran, Saudi Arabia [c] Center for Refining and Petrochemicals, Research Institute, King Fahd University of Petroleum and Minerals Dhahran, Dhahran, Saudi Arabia

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Photo-Conversion of Methane into Higher Hydrocarbons Using 355 NM Laser Radiation

M. A. Gondal,[1,*] Zain H. Yamani,[2] A. Dastgeer,[1] M. A. Ali,[3] and A. Arfaj[1]

[1]Center for Applied Physical Sciences, Research Institute,
[2]Department of Physics, and
[3]Center for Refining and Petrochemicals, Research Institute, King Fahd University of Petroleum and Minerals Dhahran, Dhahran, Saudi Arabia

ABSTRACT

A laser-based technique for the conversion of methane into higher hydrocarbons and hydrogen has been developed. This technique involves the photo-dissociation of methane using a high power pulsed ultraviolet laser at 355 nm. The reaction products, such as CH, CH_2, C_2H_2, atomic and molecular hydrogen, are characterized by real-time laser induced fluorescence for the first time, to our knowledge. In addition to this online fluorescence detection of the species, gas chromatography is also applied to analyze the stable hydrocarbon products generated due to photo-dissociation of methane. Another interesting result of the laser excitation of methane is the observation of Stimulated Raman lines

*Correspondence: M. A. Gondal, Center for Applied Physical Sciences, Research Institute, King Fahd University of Petroleum and Minerals Dhahran, Box 372, Dhahran 31261, Saudi Arabia; Fax: +966-38604281; E-mail: magondal@kfupm.edu.sa.

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(Stokes and Antistokes) observed in the 150–850 nm region, which is a manifestation of the inherent characteristics of the laser radiation such as high directionality and high intensity.

Key Words: Methane conversion; Multi-photon dissociation; Hydrocarbons; Laser photolysis.

INTRODUCTION

Methane possesses higher energy content per CO_2 molecule produced, compared to other combustion fuels such as oil and coal, because of the low C:H ratio in CH_4 molecules. Besides being a potent energy source, methane is naturally abundant with an estimated 1.4×10^{11} m^3 available in the reserves worldwide.[1,2] Hence methane, in principle, can be considered to be a potentially inexpensive source of energy.

Although methane is naturally abundant, its reserves are spread across remote and inaccessible geographic locations, and the transportation of methane, over long distances in gaseous form, is technically difficult and not cost effective with existing pipelines and transportation systems. This limits the global consumption of methane. However, if methane is converted into useful hydrocarbons in liquid form, then the existing petroleum pipeline network can be utilized for transporting methane, and hence the cost of transportation can be substantially brought down and the methane resource can be effectively used.

Another important motive for the conversion of methane into other hydrocarbons is the fact that methane is a major contributor to global warming and a hazardous green house gas.[3] The control of global warming and the reduction of green house gases, are imperative environmental concerns and these issues have been discussed in numerous international conferences on environment and many protocols have been signed by nations.[4,5] Hence, conversion of methane into useful hydrocarbons is always a welcome move for humanity in general and industrial consumers in particular. Yet another important advantage of the conversion of methane is the generation of hydrogen, which is a major component of sustainable energy systems that can play a key role in all sectors of the global economy in the future. Today, hydrogen is widely used as a chemical feedstock in the petrochemical, food, electronics and metallurgical industries. Higher hydrocarbons such as ethylene, and propylene are used as raw materials for the production of polyethylene and polypropylene.

The conventional methods of methane conversion involve multi-step reaction processes, where methane and steam are transformed into synthesis

gas (a mixture of H_2 and CO) by steam reforming, and then converted into liquid hydrocarbons through Fisher–Tropsch synthesis, which requires extreme experimental conditions such as high temperature and pressure.[6–9] Research efforts have been directed to invent alternative techniques for the direct conversion of methane into liquid fuels, chemicals and intermediate compounds. At present, there are three reported methods for methane conversion based on photo-chemical processes using conventional UV sources, plasmas and microwave energy in the presence of catalysts.[6–20]

Suzuki et al.[11] reported the formation of formaldehyde from photo-oxidation of methane over a molybdena-silica catalyst, at 463–493 K, under UV radiation. Wada et al.[12,13] found that aldehydes can be selectively produced using a range of oxides of zinc, lithium, potassium, etc. from methane to propane, at ambient to 550 K temperature, using UV radiation. Hill et al.[7] reported photo-induced reactions of methane on the surface of molybdena-silica under UV irradiation, and noted that the methane was adsorbed on the catalyst surface and, when heated from 293 to 473 K, the desorption produced considerable amounts of ethylene, ethane, hydrogen and smaller amounts of C_3 and C_4 alkenes and alkanes. Similar results were obtained using ethane as a feedstock with the same catalyst. These studies have confirmed that UV irradiation of alkanes and alkenes in the presence of catalysts is an effective and novel method to produce valuable hydrocarbons. However, we note that most of the above photochemical processes are carried out under complicated experimental conditions such as high temperature and pressure and/ or require special catalysts.

The major objective of this study is to explore the possibility of a simple methane conversion technique with laser excitation at room temperature and normal pressure without any catalyst. For this, a laser beam of 355 nm, and a specially designed reaction cell were employed. The reaction products, such as CH, CH_2 and C_2H_2 as well as atomic hydrogen (H) and molecular hydrogen (H_2) were characterized using laser induced fluorescence, while the stable products were analyzed by a gas chromatograph using a capillary column capable of separating and quantifying all hydrocarbons and hydrogen generated in the reaction. Another feature of this work is the investigation of UV Raman shifting in methane, and observation of many Stokes and Antistokes Stimulated Raman Scattered (SRS) lines in the 150 nm–850 nm region. These lines were the result of the inherent characteristics of laser radiation such as high directionality and high intensity and a few of these Stokes and Antistokes lines[21–23] have been observed for the first time, to the best of our knowledge. Converting methane into higher hydrocarbons at room temperature and normal pressures without catalysts is, in and of itself, exciting and interesting. If one is able to induce chain reactions in these non-linear conversion processes, it may be possible to inexpensively convert

methane into ethane and other compounds. However, in this paper we make no claim that this process will be economically viable. Future studies should explore the commercial aspects of this method.

EXPERIMENTAL SETUP DETAILS

A schematic of the experimental setup is presented in Figure 1. A custom made reaction chamber mounted with optical grade quartz windows at both ends is equipped with pressure and temperature sensors for monitoring and controlling the reaction conditions. The methane used for this study is high purity (99.99%) research grade. Special care has been taken to avoid any form of impurities in the cell. For this purpose, the cell

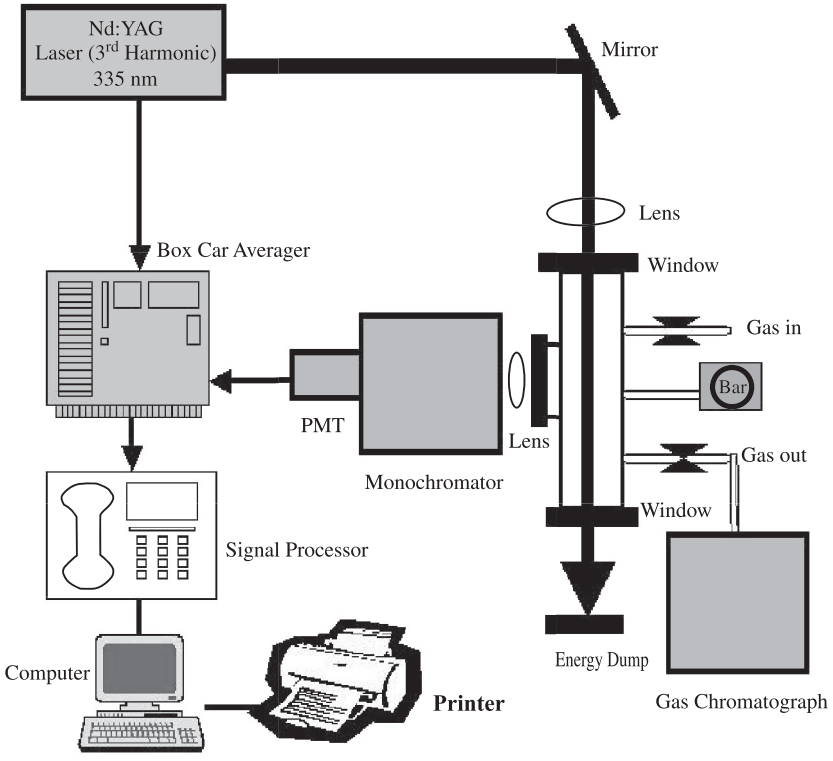

Figure 1. Schematic diagram of the experimental setup for the photo-conversion of methane using UV laser.

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was evacuated to a very low pressure (10^{-6} mbar) and leak tests over an extended time period were conducted before filling the cell with pure methane. The excitation source, a 355 nm high power laser beam, is generated from the third harmonic of a Spectra Physics Nd:YAG laser (Model GCR 250).

The reaction process has been monitored and characterized simultaneously by real-time laser induced fluorescence (LIF).[24–26] and a gas chromatographic system equipped with a capillary column in a temperature programmed oven. The fluorescence from the excited intermediate species such as CH, CH_2, C_2H_2, and hydrogen was scanned using a grating monochromator (Spex, Model 1875 with Compudrive CD 2A) equipped with a thermoelectrically cooled photomultiplier (Thorne EMI, Model 9558B). The signal was recorded by a boxcar averager (EG&G, Model 4422) and a signal processor (EG&G, Model 4402), and averaged at 10 laser pulses per sampling point, with the boxcar triggered by the Q-switch of the 10 Hz laser.

The stable reaction products were characterized using a gas chromatographic system (Shimadzu GC-17A) equipped with a capillary column in a temperature programmed oven. The hydrocarbons were detected and

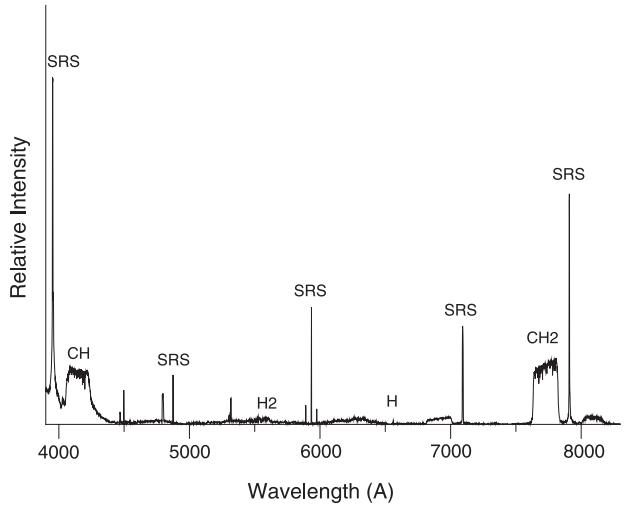

Figure 2. Fluorescence spectrum due to the photo-dissociation of methane in the 390–820 nm region due to the excitation of 355 nm. The spectral transitions due to free radicals such as CH, C_2H_2, CH_2, H, and H_2 are identified on the spectrum along with the Stimulated Raman (Stokes shifted) Scattered lines.

analyzed by a flame ionization detector while hydrogen was monitored using a thermal conductive detector. The gas chromatograph is provided with an injector and a gas loop. Gaseous reaction products were injected through the loop into a capillary column where different components were separated. Prior to injecting the sample, standard gas mixtures were chromatographed to determine the retention times and response factor of each component under the selected analysis conditions.

RESULTS AND DISCUSSIONS

Laser Induced Fluorescence (LIF) spectra of methane in the 390–820 nm and 150–350 nm regions, excited by 355 nm laser radiation, are presented in Figure 2 and Figure 3 respectively. These spectra show the species such as CH, CH_2, C_2H_2 as well as traces of atomic (H) and molecular hydrogen (H_2) generated due to the photochemical processes of methane. Both spectra were taken at room temperature and the pressure was

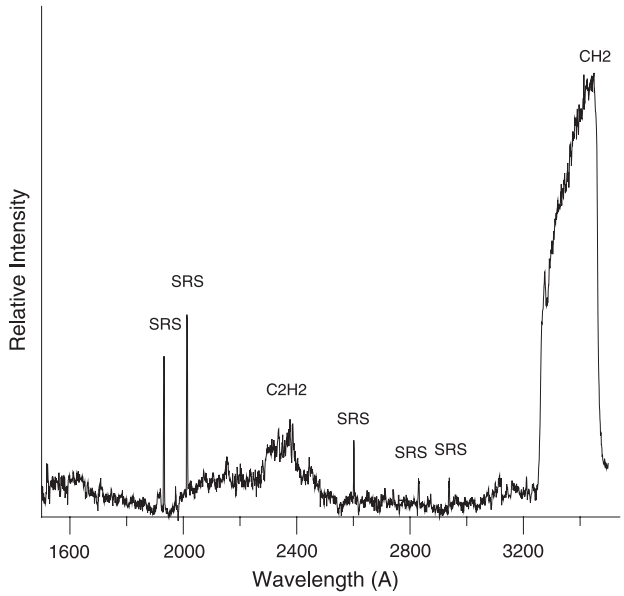

Figure 3. Typical fluorescence spectrum recorded in the 150–350 nm region by the excitation of CH_4 with 355 nm. Stimulated Raman (AntiStokes shifted) Scattered lines are marked on the spectrum.

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kept at 1 atmosphere. Since methane is transparent at 355 nm, any photo-dissociation must have taken place by a multi-photon process. It should be noted that previous work on multi-photon dissociation in organic compounds focused on free radicals and not on the production of higher hydrocarbons.[27,28]

A few possible photochemical reaction pathways of methane excited by 355 nm laser radiation are outlined below. The selective laser excitation converts methane molecules into methylene and methyl radicals which will further react together to produce C_2 and C_3 hydrocarbons.

$$CH_4 + \text{n h}\nu \text{ (UV laser)} \Rightarrow CH_3 + H$$

$$H + H \Rightarrow H_2 \text{ (Hydrogen Production)}$$

$$CH_4 + \text{n h}\nu \text{ (UV laser)} \Rightarrow CH_2 + H_2$$

$$CH_2 + CH_2 \Rightarrow C_2H_4 \text{ (Ethane production)}$$

$$C_2H_4 + CH_2 \Rightarrow C_3H_6 \text{ (Higher Hydrocarbons)}$$

Table 1 shows the wavelengths of the spectral emission lines and their spectral assignments. These assignments have been made using the tables of spectral lines for these species published in the literature.[29–32] The following emission lines have been identified from Figure 2 and Figure 3:

- the Balmer atomic hydrogen emission line H_α at 656.2 nm
- the Fulcher molecular hydrogen bands α ($d^3\Pi u$-$a^3\Sigma g$) mainly dispersed over the 590–640 nm region.[29]
- The CH ($B^2\ \Sigma$-$X^2\ \Pi$) system dispersed over 403–480 nm region[30] and CH ($A^2\ \Delta$-$X^2\ \Pi$) with the Q (0,0) band head at 431 nm[31]
- The CH_2 ($b\ ^1B_1$-$a\ ^1A_1$) system dispersed over 660–900 nm[29]
- The C_2H_2 ($A\ ^1A_u$-$X^1\Sigma g$) system dispersed over 210–238 nm[32]

In addition to these emission lines, many lines attributed to the Stimulated Raman Scattering (SRS) of methane can also be noticed as in Figure 2 and Figure 3.

The frequency of the scattered photon is $\omega_{SRS} = \omega_o + \omega_{mn}$ where ω_o is the frequency of incident photon which in our case is 28169 cm^{-1} (for 355 nm) and ω_{mn} is the molecular transition frequency. From the observed wavelength of the strongest Stokes line at 395.9 nm, the molecular

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Table 1. Lines observed in the 150–850 nm region by photo-dissociation of methane with 355 nm laser.

	Wavelength (nm)	Relative intensity	Assignment
1	193.9	37	SRS^{++}
2	202.0	46	SRS^{++}
3	237.6**	22	C_2H_2
4	260.9	17	SRS^{++}
5	283.7	7	SRS^{++}
6	294.5	7	SRS^{++}
7	334.4**	77	CH_2
8	395.9	1000	SRS^{+}
9	403.6	76	CH
10	412.7	148	CH
11	447.6	35	SRS^{+}
12	450.5	98	SRS^{+}
13	479.4	87	CH
14	486.2	141	H
15	532.0	73	Laser (II harmonic)
16	555.9**	16	H_2
17	589.8	54	SRS^{+}
18	594.2	336	SRS^{+}
19	598.2	43	SRS^{+}
20	628.2	13	H_2
21	656.2	10	H
22	691.1**	14	CH_2
23	710.0	283	SRS^{+}
24	771.9**	190	CH_2
25	791.7	664	SRS^{+}
26	808.8**	15	CH_2

**Center of the molecular Band system.
+SRS-Stimulated Raman Scattering (Stokes Lines).
++SRS-Stimulated Raman Scattering (Antistokes Lines).

transition frequency ω_{mn} is calculated to be 2915 cm^{-1} which fits very well with the ν_1 fundamental vibrational modes of CH_4.[22] Table 1 lists the peaks observed in the LIF measurements in the 150–850 nm region.

It is worth mentioning that the observed SRS lines possess the characteristics of the laser beam such as high intensity, low beam divergence and Gaussian shape beam spot. The SRS signals were recorded in the backward direction through a dichroic mirror in order to avoid the

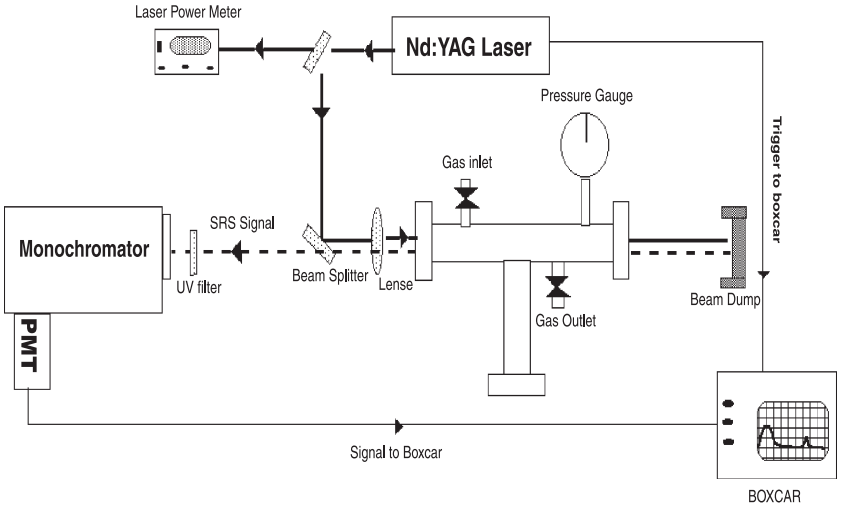

Figure 4. Schematic diagram of the experimental setup for recording of SRS lines in the backward direction.

detection of laser radiation scattered by methane molecules, as shown in Figure 4.

In order to explore the excitation mechanism for Stimulated Raman Scattering of methane, the energy dependence of the SRS signal at 395.9 nm was measured. The log–log plot of fluorescence intensity versus the laser energy gave a slope of 2.96, indicating a non-linear three-photon process. A detailed study of these SRS lines is in progress and will be reported in a separate paper.

In the photo-chemical reactions described above, both atomic and molecular hydrogen are generated through multi-photon photo-dissociation of methane and its presence is slightly evident in Figure 2. As one of our objectives of this study is to study the production of hydrogen through the photochemical reactions of methane, we tried many experimental conditions to enhance the production of hydrogen and noticed that atmospheric pressure and room temperature are the optimum conditions for the generation of hydrogen. Figure 5(a) shows the laser induced fluorescence (LIF) H_α line of hydrogen (656.2 nm) recorded by 355 nm laser excitation of the CH_4 sample. Figure 5(b) is the LIF signal of pure hydrogen gas. The cell pressures for both hydrogen and methane were 1 atmosphere; other experimental conditions were also identical for both spectra in Figure 5. In

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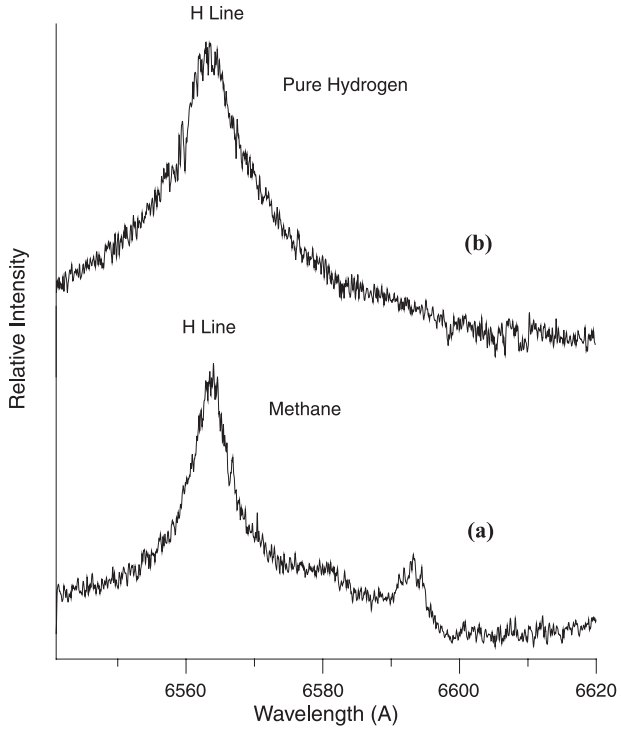

Figure 5. H_α line recorded at 656.2 nm with 355 nm laser excitation. (a) Spectrum of hydrogen generated due to photo-dissociation of methane. (b) Spectrum of pure hydrogen generated due to photo-dissociation of pure H_2.

Figures 5(a) and 5(b), both spectra are identical with respect to all their features except the signal intensity. This is attributed to the fact that emission is naturally more intense from the pure hydrogen than the emission from hydrogen generated from photo-dissociation of methane.

Figure 6 shows a typical gas chromatogram based on the calibration of known compositions of the expected species. The sample was analyzed after one hour exposure to 355 nm laser radiation, with energy of about 50 mJ/pulse. The stable compounds generated due to the photo-conversion of methane are Ethane, Ethylene, Propane, C_4 Butane, Isobutane and Isopentane. It should be emphasized that these higher hydrocarbons were generated without any catalysts. However, we believe that the yield and selectivity of the byproducts (higher hydrocarbons) can be enhanced by using suitable catalysts and by optimizing the experimental conditions such as excitation wavelength, laser power, gas temperature and pressure inside

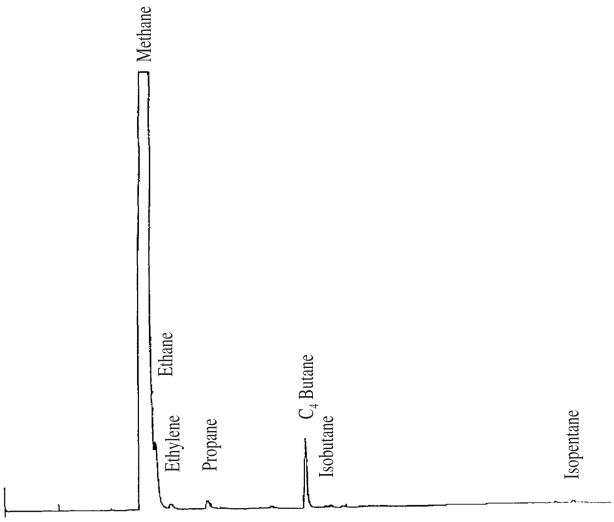

Figure 6. Chromatogram of the photo-conversion of methane with 355 nm lasers. Various species generated by conversion of methane under the influence of laser are shown.

the reaction chamber. The study on the effects of photo-catalysts and other experimental parameters in enhancing the yield in the production of higher hydrocarbon will be carried out in the near future.

CONCLUSIONS

This work demonstrates the conversion of methane into higher hydrocarbon products such as ethane, butane and pentane, by 355 nm UV laser excitation at room temperature. No attempt was made in this study to explore the commercial viability of this method, as this was not the main objective of this study. Another important result obtained in this study is the detection of atomic and molecular hydrogen through the photo-dissociation of methane. Stimulated Raman Scattered lines (Stokes and Antistokes) over a broad spectral range have also been recorded. The energy dependence of a strong Stokes line indicated that it is a three photon process. As these SRS lines possess the characteristics of the laser radiation, there is a prospect of building a tunable laser over a broad spectral range in the vacuum UV(150–250 nm) in the future for various applications in the field of the environment, spectroscopy and medical diagnostics.

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