Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 156 (2016) 118–122

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Possibility of methane conversion into heavier hydrocarbons using nanosecond lasers

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ARTICLE INFO

Article history:
Received 28 February 2015
Received in revised form 17 August 2015
Accepted 20 November 2015
Available online 21 November 2015

Keywords:
Dissociation
Conversion mechanism
Methane
Nanosecond lasers
Ion-neutral reactions

ABSTRACT

Effect of nanosecond lasers on the methane dissociation is experimentally studied by using three different laser wavelengths at 248 nm, 355 nm and 532 nm. C_2H_2 generation is measured as a major reaction product in experiments and the energy consumptions in production of this component are measured as 5.8 MJ/mol, 3.1 MJ/mol and 69.0 MJ/mol, for 355 nm, 532 nm and 248 nm wavelengths, respectively. The mechanism of conversion and production of new stable hydrocarbons is also theoretically investigated. It is found that in theoretical calculations, the ion-molecule reactions should be included and this leads to a unique approach in proper explanation of the experimental measurements.

1. Introduction

Strong laser field interaction with molecules is a very exciting subject for many aspects, especially controlling chemical reactions [1,2]. Irradiation of molecules by strong optical field readily leads to breaking one or more molecular bonds and molecular processes such as ionization and conversion of fragments into the favorite products [3–5]. Several mechanisms are used to explain the photo-dissociation of molecules in intense laser fields. Some methods such as multiphoton ionization (MPI), above threshold ionization (ATI), field ionization (FI), coulomb explosion (CE), and explosive photo-dissociation are proposed [6–10]. At the ultra-intense elliptically polarized laser fields, the molecular alignment and angular dependence of the ionization probability present a major effect on the ionization processes [11–13]. The old dream of comprehension of the molecular dynamics and controlling of reactions towards desired valuable products among other competing components became transparent by real time observations of the transition-state region between reagents and products in 1988 [14]. Using the advanced intense femtosecond laser pulses with pulse shaping technology, the objective of controlling chemical reactions and optical spectroscopy with coherent light are implemented [15–18]. The capability of ultrashort laser pulses allowed the probe of reaction dynamics at a real time of nuclear motion and the direct observation of molecular orientation [19–20].

Methane, the most stable hydrocarbon at room temperature, is one of the major greenhouse gases with very high global warming potential. Indeed, the global warming potential of CH_4 is very high for UV absorption and IR emission and on a mass basis it is 25 times that of CO_2 over a 100-year time horizon [21]. Although, methane is a clean and primary fossil fuel, the conversion of methane into higher hydrocarbons and hydrogen gas hydrocarbons is the goal of many nations including the oil and gas fields [22,23]. In addition, the transportation of methane across distant and remote geographic regions is a main challenge, which may be resolved by conversion methods. Moreover, mechanism of onsite liquefaction of methane can prevent contributing to the generated greenhouse gases [24,25].

The conversion of natural gas to hydrocarbons has not yet been successfully economized in an inexpensive process. In general, there are two types of indirect and direct techniques for methane conversion to hydrocarbons. The indirect route for methane conversion (e.g. Fischer–Tropsch) requires the production of synthesis gases (CO and H_2) from methane by expensive and inefficient process of steam reforming. The direct ways are not accepted since to date it has not been possible to achieve considerable conversion yield to heavier hydrocarbons, directly [26–28]. The photo-catalytic conversion techniques have some advantages including partially selecting and low temperature processing of some desired chemical products which has motivated the scientist attention to solve the problems of direct methods in conversion processes [29,30]. Experimental irradiations of CH_4–C_2H_2 gas mixtures using UV lasers have been carried out in order to test the catalytic scheme of dissociation of methane via the photolysis of acetylene [31]. By analyzing the dependence of the stable fragments on laser

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http://dx.doi.org/10.1016/j.saa.2015.11.018
1386-1425/

parameters such as irradiation time, it is shown that the stable products of C_2H_2, C_2H_4, and C_2H_6, appear in constant amounts in the different irradiation times. However, this is not a cost effective approach and valuable catalysts waste during the process. As a result, some other techniques should be explored.

One of the important parameters in the conversion method is the energy consideration which determines the cost effectiveness of the process. Since femtosecond lasers with unique capabilities of delivering the minimum required energy for breaking the favorite bond, as mentioned above, may be the best candidate in this regard. The experimental setup is supplied by a complex system and computer equipped with the genetic algorithm code. Although, great improvements are achieved in controlling chemical reactions; by these methods, initial experimental data for genetic and learning is needed and is not an economical method. However, In spite of the femtosecond lasers capabilities, nanosecond lasers become a powerful tool in dissociation of chemical reactions. These lasers are inexpensive, accessible sources and can have optimum energy consumption in the conversion process. Due to these valuable features there have been considerable attentions on the application of these lasers in this field. Few fundamental studies are concentrated on the interaction of intense laser fields with molecules using nanosecond lasers [24,32–34]. Since, the photo-dissociation of methane has been studied extensively based on the theoretical approaches [35,36]. Some studies focused on recombination mechanisms in production of higher hydrocarbons [37]. In earlier reports it is supposed that the laser induced methyl and methylene radicals constitute the building blocks of higher hydrocarbons [38,39].

Following our recent studies on dissociation of methane [35,40], in the present work the conversion process of methane is experimentally implemented by using three different wavelengths of 248 nm, 355 nm and 532 nm and a reaction theoretical model is proposed. The main aim is to present a comprehensive conversion mechanism for production of the stable valuable products. Basically, lasers do not considerably increase the temperature inside the reaction chamber and can be an appropriate candidate economically. To the best of our knowledge there is no complete reported consistent conversion model experimentally in this field. Furthermore, a useful theoretical model is proposed which properly explained the experimentally obtained yields. This is explained in detail in the following.

2. Experimental setup

Fig. 1 shows a schematic experimental setup which is similar to the earlier reported system [40]. The reaction chamber is a cylindrical aluminum chamber with an internal diameter of 3 cm and a length of 10 cm, which gives about 71 cm^3 volume. All of the chamber volume was filled with methane in 870 mbar for 248 nm and 355 nm laser experiments; however, the effective volume was decreased to 10 cm^3 for 532 nm in order to decrease the laser energy consumption. It should be noted that the decrease of reaction volume does not affect the consumed specific energy per mole (J/mol) of produced components, because the reactions occur in a small volume around the focal point.

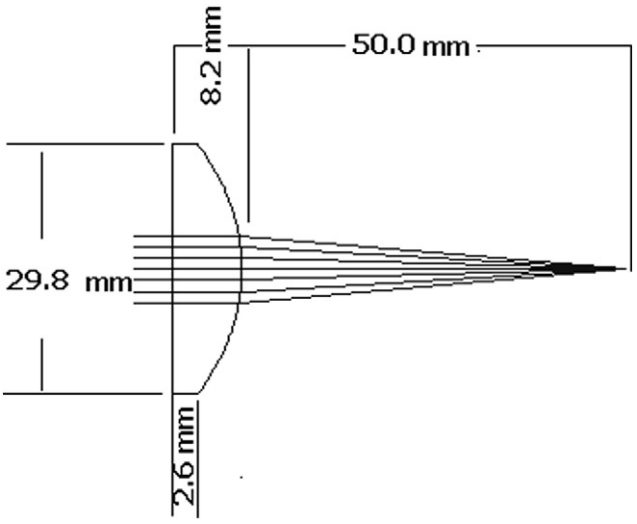

Fig. 2. The geometrical properties of plane-convex lens used in experimental setup for focusing laser beam. The focal length of the lens is about 50.0 mm and the direction of incident beam is as shown in the figure.

The laser beam is focused by fused silica lens of Fig. 2, longitudinally through quartz window at the center of the cell. Two mass flow controllers are used to evacuate the reaction chamber by a vacuum pump in order to fill it by proper methane gas. A gas chromatograph (GC) series B 5890 equipped with packed column and a Flame Ionization Detector (FID) is used to analyze the reaction products. Helium was used as a carrier gas and acetylene, ethylene and ethane were used as references. The reactor was evacuated to below 0.001 Pa and then pressurized with research-grade (99.999%) methane gas. Following the laser exposure, the reactor content was injected into the packed column of GC and the concentrations of final stable products were measured.

3. Experimental results

In conversion process three different nanosecond lasers were used in experiments. The characteristics of lasers are listed in Table 1. Focal spot sizes of the beams are estimated using the *ZEMAX* optical software package.

Fig. 3 depicts the fluorescence spectrum of photo-dissociation of methane as a function of wavelength in the 200–1000 nm region induced by second harmonic Nd:YAG laser at 532 nm irradiation. The existence of 532 nm wavelength is due to the scattering of laser light into detector. Other lines correspond to the unstable products formed after laser absorption process.

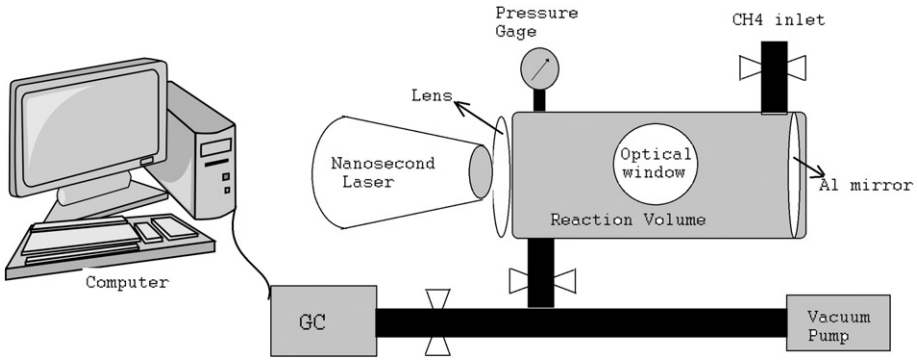

Fig. 1. Schematic view of the experimental setup.