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Production of Hydrogen Molecule from Methane Molecule Amplified with Excitation of Anti-Symmetric Modes of Vibration

Sinan ERDOGAN *1

Abstract

Some factors, such as pressure and temperature, affect the rate of chemical reactions. In addition, the activation energy barrier must be overcome for the reaction to be initiated. It can be preferred to overcome this barrier by using catalysts and preheating. The catalyst ensures that it obtains the energy to react quickly by transferring it to the reactants. Similarly, the translational, vibrational, and rotational energy levels of reactants can be increased by preheating. According to the kinetic molecular theory of gases, preheating increases the kinetic energies of the gases and the speed of their collision, so the reaction takes place faster. This study theoretically investigates possible reactions of methane that can occur with the effect of only vibrational energy levels. The vibrational excitation of the molecules affects the reaction rates, and the activation barrier is overcome with lower energies. Using laser-based techniques makes the excitation of well-defined vibrational modes possible. This study investigated inelastic collisions of a methane molecule with well-characterized energy levels in infrared spectroscopy with some gases and the vibrational energy transfers that occur in these collisions. The methane molecule is the simplest form of a molecular structure consisting of more than three atoms of hydrogen atoms, which play an essential role in combustion chemistry. It shows that C—H stretch excitation increases the reaction rate of methane (CH_4) molecules.

Keywords: Methane, molecular vibration, energy transfer, vibrational spectroscopy

1. INTRODUCTION

The importance of hydrogen is increasing day by day with the development of new technologies. The widespread use of hydrogen-powered vehicles, especially in transportation, is crucial for accelerating the global energy transformation. In this energy conversion process, studies on clean hydrogen production, storage of hydrogen, and getting maximum efficiency from hydrogen have gained momentum.

It has become the primary goal to produce energy without burning and creating harmful emissions. Even though almost all the hydrogen production is provided from fossil fuels, studies on clean hydrogen production have increased in recent years [1-3].

Traditional hydrogen production methods from fossil fuels, such as (1) steam reforming of natural gas, (2) partial oxidation of methane, and (3) coal gasification, are prominent. Other methods are (4) biomass gasification and (5) electrolysis methods [1].

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Recent research has focused on enhancing hydrogen production by the direct thermocatalytic decomposition of methane to form elemental carbon and hydrogen as an attractive alternative to the conventional steam reforming process [4]. Thermodynamically, the reaction of $CH_4(g) \rightarrow C + 2H_2(g)$ can occur from 543°C, but kinetically, the reaction becomes dominant from 800°C without any catalyst [5]. Methane decomposition is a moderately endothermic reaction. Due to the strong C–H bonds, non-catalytic thermal cracking of methane requires temperatures higher than 1200 °C to obtain a reasonable yield experimentally [4].

The use of solar radiation as a heating source to achieve high temperatures has been studied in recent studies. Hirsch and Steinfeld [6] investigated using concentrated solar radiation as the source of high-temperature process heat. They determined that the conversion of methane was 67% at 1327 °C and 1 atm. Dahl et al. [7] obtained that the conversion of methane was 90% at 1860 °C using concentrated solar energy as a heating source.

Maag et al. [8] calculated methane conversion and hydrogen yield exceeding 95% at 1027-1327 °C with solar energy.

In a study, hydrogen was produced through a thermal decomposition reaction by injecting methane gas into a molten slag obtained in the metal industry. The decomposition reaction sequence is expressed as $CH_4(g) \rightarrow CH_3(\text{radical}) \rightarrow CH_2(\text{radical}) \rightarrow CH(\text{radical}) \rightarrow C\ (\text{soot})$ [5].

Using a catalyst can significantly reduce the reaction's temperature [4]. Traditionally, methane decomposition has been catalyzed by nickel, copper, iron, and some noble metals [9].

In a study using a Ni-based catalyst at a temperature of 700°C, it was calculated that the concentration of H_2 was around 80%, corresponding to a methane conversion close to the theoretical equilibrium value [10]. On the contrary, Fe catalysts can decompose methane at a temperature range of 700-1000°C [11]. Methane conversion was not as high when methane decomposition was performed below 600°C.

As seen in the studies, hydrogen can be produced from methane at high temperatures. However, developments in quantum mechanics in recent years have revealed that some chemical reactions can be carried out without reaching high temperatures.

The chemical industry has discovered in recent years that chemical reaction rates or efficiency have been increased by ultrasound-assisted technologies [12]. In addition, studies on the effect of microwave-assisted reactions on mass and heat transfer have risen in recent years [13]. These exciting developments make it necessary to examine chemical reactions from the perspective of quantum mechanics.

From this perspective, researchers study molecular motions. The different types of molecular motion are translation, rotation, vibration, and electronic motion. The translation motion occurs from the center-of-mass motions of molecules. The electron configuration of the system defines an electronic state, and each electronic state corresponds to one of the molecule's energy levels. Electronic motion defines transitions between different electronic states. The vibrational transitions occur between different vibrational levels of the same electronic state. Rotational transitions occur mainly between rotational levels of the same vibrational state. The number of independent ways a molecule of gas can move is called the degree of freedom [14].

Some related research in molecular motions is as follows. Huarte-Larrañaga and Manthe [15] investigated the reaction between methane molecule and hydrogen atom regarding quantum mechanics. Palma et al. [16] studied the rate constants of the CH_4+H reaction and investigated the transition of the vibrational energies of the reacting CH_4 molecule to the CH_3 molecule during the reaction. Camden et al. [17] investigated the effects of C—H stretching excitation of CH_4 molecule on the reaction with hydrogen. Simpson et al. [18] investigated the reaction mechanism of atomic chlorine with vibrationally excited CH_4 and CHD_3 molecules. Bourcin et al. [19] investigated the rotational relaxation and vibrational energy transfer processes that occur in inelastic collisions of methane with H_2 and He at -80°C and 23°C. Corchado et al. [20] discussed the reaction of CH_4 and H atom in terms of energy surface area to obtain a hydrogen molecule. Another study presented the investigation of rovibrational transitions of methyl radicals (CH_3, CD_3) by infrared spectroscopy [21].

This study discusses preparing suitable conditions for reactions with electromagnetic (EM) waves by considering molecules' vibrational excitation energy levels. In addition, the behavior of the fundamental ($v_3=0\rightarrow1$) and overtone ($v_3=0\rightarrow2$) levels of the CH_4 molecule under vibrational stimulation was investigated. In addition, inelastic collisions of a vibrationally excited CH_4 molecule with hydrogen with specific kinetic energy were aimed, and the breaking of chemical bonds and the formation of new bonds as a result of this collision were discussed.

2. TEORY AND METHOD

In this section, the basic information for the theoretical design of the study is given. Especially the vibration modes of methane, the kinetic theory, the theory of inelastic collision, and the chemical reactions formed the infrastructure of this study.

2.1. Vibration Spectroscopy and Vibration Modes of Methane

The molecule or the atoms that make up the molecule are continually motion. These are the translational motion of the molecule, rotational motion around an axis, periodic changes in the length of a chemical bond, or vibrational movements that cause periodic changes in the angles between the atoms that make up the molecule [14]. Differences in translational, rotational, and vibrational energy levels indicate that molecules differ in their energies. These differences reveal the molecule's absorption, emission and reflection properties by molecular spectroscopy techniques. EM waves that cause vibration and rotational movements of the molecule are located in the infrared region of the electromagnetic spectrum and are examined by infrared spectroscopy [22]. The molecule is stimulated to an upper or two higher vibrational levels and raises its energy level by absorbing the energy of EM waves. The electric field of EM waves acts on the molecule and further strengthens one of the molecular motions [19].

It is easy to determine the vibrational modes of diatomic or triatomic molecules and the energies they absorb. However, making these calculations for polyatomic molecules becomes problematic depending on the atomic number. Methane gas, the smallest molecule containing more than three atoms, has been investigated within the scope of this study. With the increase in the number of atoms, many vibrational centers are formed, and there are various interactions between these centers. All effects must be taken into account in the calculations. The vibrations between atoms can be collected in two classes. These are stretching and bending vibrations. Stretching vibrations occur when the distance between two atoms constantly changes along the bond axis of the atoms. It has two sub-modes as symmetrical and asymmetrical stress. Bending vibrations result from changing the angle between two bonds and have four modes; scissoring, rocking, wagging, and twisting modes [23].

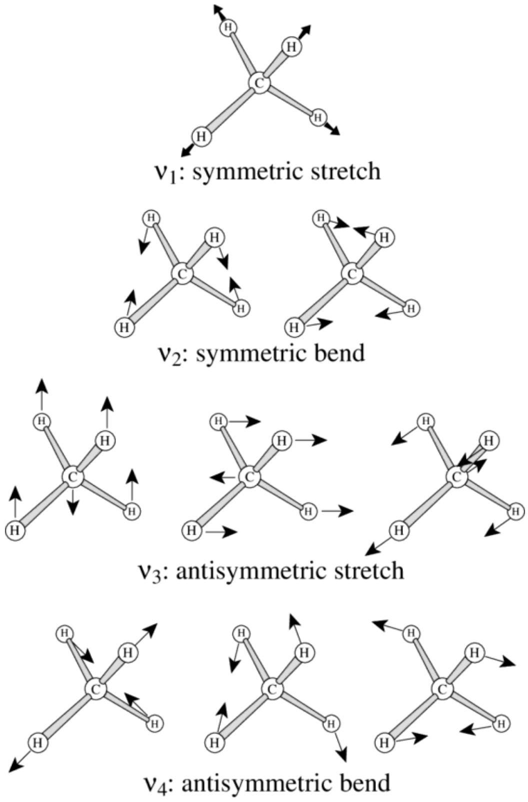

Figure 1 Vibration modes of methane [24]

The degree of freedom of a molecule with N atoms is 3N, and the total degree of freedom of the CH_4 molecule is 15. These modes belong to translational movements, three modes to rotation, and the remaining nine modes belong to vibrational motions. The vibrational modes of the CH_4 molecule are shown in Fig.1.

The vibrational modes of the methane molecule are called v_1, v_2, v_3, and v_4. The v_3 and v_4 vibration modes have three different energy levels, while the v_2 vibration mode has two different energy levels. The energy levels of these vibrational modes are 2917 cm^{-1} (*in terms of energy, its value is 34.90 kJ/mol; 0.36 eV*) for v_1, 1533 cm^{-1} (*18.34 kJ/mol; 0.19 eV*) for v_2, 3019 cm^{-1} (*36.12 kJ/mol; 0.37 eV*) for v_3, and 1311 cm^{-1} (*15.68 kJ/mol; 0.16 eV*) for v_4, respectively [17].

2.2. Kinetic Theory and Chemical Reactions

The energies of molecules change especially with movements such as translation, rotation, and vibration. As the energy levels of molecules excited by vibration rise to higher levels, the molecule's energy significantly increases. Gaseous molecules freely collide with each other and can transfer their energy to other molecules. Suppose the total energies of the two vibrationally excited molecules are equal to the energy required for a molecule to rotate. In that case, the collision occurs in an inelastic manner, and the motion modes of the molecules can change with the energy transfer [25]. If the molecules collide with collision energy below the energy level required for the molecules to absorb, they will bounce off each other by making elastic collisions. With inelastic collisions, the potential energies of the molecules can turn into kinetic energy, or their kinetic energies can turn into potential energy. According to the kinetic theory, molecules with increased kinetic energies tend to collide more with other molecules. When molecules collide inflexibly, the kinetic energy of the molecules can be used to stretch, bend, and eventually break bonds that lead to chemical reactions [19]. Thus, chemically, atoms or smaller groups of molecules in the molecule begin to separate.

There is a specific energy required for molecules to break existing bonds during a chemical reaction [26]. As it is known, the minimum energy requirement that must be met for a chemical reaction to take place is called activation energy [27]. The elementary reaction of the decomposition of CH_4 to CH_3 is $CH_4(g) \rightarrow CH_3 + H$ which activation energy is 264-430 kJ/mol [5]. For chemical reactions to begin, the activation energy barrier must be overcome, and molecules or atoms must collide with the correct orientation. If the molecules move too slowly with too little kinetic energy or collide in the wrong direction, they do not react and bounce off each other in an elastic collision. However, some methods are being developed to increase the collision numbers of molecules. In this method, the direction of the molecules is adjusted according to the permanent dipole moment under an electric or magnetic field. Thus the reaction rate can be increased by providing more precisely oriented collisions [28] Therewithal, reactions can be initiated with lower activation energy by lowering the energy barrier by using a catalyst [29]. The activation energy of $CH_4(g) + H \rightarrow CH_3(g) + H_2(g)$ reaction with radical hydrogen is 45-60 kJ/mol [5].

Consequently, molecules with an energy above the low energy barrier will tend to react. This effect will increase the reaction rate. With another method that has been tried in recent years, the vibrational energy levels of molecules are stimulated using EM waves, and the molecule rapidly reacts by transferring its energy to another molecule during collisions. These methods pull down the activation energy barrier, allowing more molecules to react even at low temperatures [30-32].

Hydrogen separation from methane gas has recently been a suitable prototype for the theoretical study of bimolecular reactions due to its relatively small size, and its chemical reaction is as follows.

$$CH_4 + X \rightarrow CH_3 + HX \qquad (1)$$

There are several theoretical and experimental studies in the literature that deal with the collision reactions of the X atom, such as Cl, O, or H [18, 19].

3. THEORETICAL DESIGN OF HYDROGEN PRODUCTION FROM AN EXCITED METHANE

The accelerated H atoms are produced by the UV photolysis of HBr, and the antisymmetric stretching fundamental or overtone of methane is prepared by direct infrared absorption.

Accelerated hydrogen atoms are obtained by photolysis by sending EM radiation with a 200-230 nm wavelength in the ultraviolet (UV) region onto the hydrogen bromide (HBr) molecule [17]. Thus, the H atom will acquire translational kinetic energy.

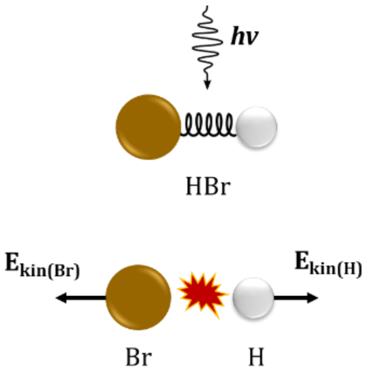

Figure 2 Dissociation of the HBr molecule

The atoms move away from each other at certain speeds by sending an EM beam located in the UV region to the HBr molecule. Thus, the HBr molecule dissociates into H and Br atoms as shown in Fig. 2 [33]. The balance of energy changes due to bond dissociation of the HBr molecule by the laser beam is shown in Eq.2 [34].

$$hv + E_{int(HBr)} = D_0 + E_{kin(Br)} + E_{kin(H)} \qquad (2)$$

The dissociation energy of the Br molecule is D_0=3.75 eV [35]. The internal energy of the HBr ($E_{int(HBr)}$) molecule is negligible at 25°C [34]. In this case, the energy of the EM radiation will be spent for the two atoms to gain kinetic energy and scatter in opposite directions. The kinetic energies they gain will be proportional to their masses ($E_{kin}=mV^2/2$). In this case, the kinetic energy that hydrogen will gain will be $E_{kin(H)}$=2.27 eV if the incoming photon is a laser beam with a wavelength of approximately 205 nm, while $E_{kin(H)}$=1.63 eV in the case of a laser beam with a wavelength of approximately 230 nm.

The parametric conversion of Nd:YAG (Neodymium-doped Yttrium Aluminum Garnet) laser radiation (λ = 1.064 μm) in nonlinear crystals is a promising means of generating tunable radiation. KTP ($KTiOPO_4$-Potassium Titanyl Phosphate) can be used as a nonlinear optical crystal with excellent nonlinear, electrooptical, and acousto-optic properties. It was shown that the KTP crystal had attractive potentialities for a highly efficient parametric light generator tunable in the eye-safe region of the spectrum since this crystal possesses appropriate tuning characteristics in the IR and visible regions (0.3-4.5 µm). In addition, a nonlinear β-BaB_2O_4 (BBO-Beta-Barium Borate) crystal can also be used for this purpose [36]. The schematic diagram for the Nd:YAG is shown in Fig.3.

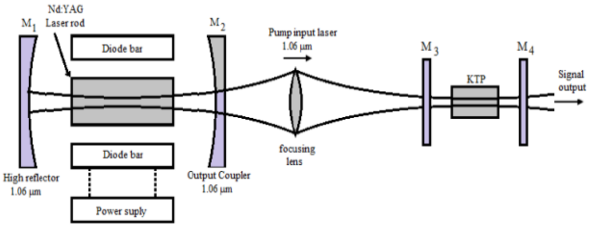

Figure 3 Schematic diagram for the Nd:YAG eye safe laser system [37]

The proposed initial reaction is the inelastic collision of the excited CH_4 molecule with the accelerated hydrogen shown in Eq.3.

$$CH_4{}^{*} + \vec{H} \rightarrow CH_3 + H_2 \tag{3}$$

In this reaction, $\vec{H}$ represents the accelerated hydrogen atom with a specific kinetic energy. $CH_4{}^{*}$ indicates an excited methane gas. The excitation will be performed on v_3 vibration mode. As a result of the absorption of asymmetric stretching modes in methane by electromagnetic radiation at wavelengths of 1.7 µm and 3.3 µm in the infrared region, the vibration mode is excited to $v_3=2$ and $v_3=1$ energy levels, respectively.

The change in the total energy of the reaction in Eq.3 is the sum of the impact energy of hydrogen on methane and the vibrational energy increased by excitation (Eq.4).

$$\Delta E_{tot} = \Delta E_{coll} + \Delta E_{vib} \tag{4}$$

The collision energy was determined as 1.63 eV and 2.27 eV, and it was calculated that 0.37 eV should be given to increase the vibration energy level to the first level and 0.74 eV to increase the energy level to the second level with the stimulation of the v_3 anti-symmetric stress mode.

The sum of the collision energy of 1.63 eV and the energy given by stimulating the C—H bond anti-symmetric stretching mode to the first level ($v_3=1$) becomes 2.00 eV. The sum of the same collision energy and the excitation energy to the second vibrational level ($v_3=2$) of the C—H bond is 2.37 eV. In case of higher collision energy (2.27 eV) accelerated hydrogen collides with CH_4, the changes in total energies according to the excitation levels are 2.64 eV for $v_3=1$ and 3.01 eV for $v_3=2$, and the related reactions are given in Eq.5-7.

$$CH_4{}^{(v=0)} + \vec{H} \rightarrow CH_3 + H_2 \tag{5}$$

$$CH_4{}^{*(v_3=1)} + \vec{H} \rightarrow CH_3 + H_2 \tag{6}$$

$$CH_4{}^{*(v_3=2)} + \vec{H} \rightarrow CH_3 + H_2 \tag{7}$$

The possible reactions as a result of the processes are as follows. According to reaction (5), CH_4, whose vibrational level is in the ground state, collides with accelerated hydrogen. This way, hydrogen can be separated from the methane and combined with the other hydrogen. In addition, the CH_3 molecule can also exit the reaction in the ground state. According to reaction (6), methane excited to the $v_3=1$ vibration mode can collide with accelerated hydrogen. The combined energies of both reactants can make the reaction occur. As a result, CH_3 molecule and H_2 molecule can be formed in fundamental vibrational mode. In reaction (7), methane excited to $v_3=2$ vibrational mode collides with accelerated hydrogen. As a result of this reaction, the CH_3 molecule and H_2 molecule will be formed in the ground state.

The energy level of the v_1 vibrational mode of the CH_3 molecule is 3004 cm^{-1}, $v_2=606$ cm^{-1}, $v_3=3161$ cm^{-1} and $v_4=1400$ cm^{-1} [17]. The energy level of the $v_1=1$ vibrational mode of the CH_3 molecule is 3004 cm^{-1}, which is very close to the energy level of the v_3 vibrational mode of methane (3019 cm^{-1}). For this reason, it seems possible that a methyl molecule whose v_1 vibration mode is excited by an inelastic collision can also be formed.

In addition, during the collision during the reaction, the energy of the v_3 anti-symmetric stretching mode of the methane can be transferred to the methyl formed so that the v_1 symmetrical stretching mode of the methyl molecule remains in an excited state. Eq.8-9 show the reactions for these probabilities.

$$CH_4{}^{*(v_3=1)} + \vec{H} \rightarrow CH_3{}^{*(v_1=1)} + H_2 \qquad (8)$$

$$CH_4{}^{*(v_3=2)} + \vec{H} \rightarrow CH_3{}^{*(v_1=1)} + H_2 \qquad (9)$$

According to the reaction (8), the accelerated hydrogen collides with the methane excited to the $v_3=1$ vibration mode. In this way, one hydrogen can be separated from the methane and combined with the other hydrogen. In addition, the CH_3 molecule can also exit the reaction by being excited to the $v_1=1$ vibrational mode. Another alternative reaction (9) is that methane excited to $v_3=2$ vibrational mode reacts with accelerated hydrogen to form CH_3 excited to $v_1=1$ vibrational mode, and H_2.

4. DISCUSSION AND CONCLUSION

CH_4 contains four powerful localized C—H bonds, and the bond energy of H—CH_3 was determined to be 439.3 kJ/mol under standard conditions [38]. There are conventional methods to break this H—CH_3 bond, but these can take place at very high temperatures or overvoltages. Although the steam reforming method is the cheapest hydrogen production method, it is formed by reacting water vapor between 700 and 1000 °C and natural gas with a nickel catalyst. The most basic by-products of this reaction are CO, CO_2 and other greenhouse gases. In electrolysis, another prominent method, overvoltages in the system increase the cost of this method. Although this method takes place at low temperatures, the cost is high. In these methods, the energy levels of the molecules increase and when the energy level exceeds the activation energy, the reaction takes place.

The v_3 vibrational mode is excited to the first energy level by giving 0.37 eV energy to the methane molecule at a wave number of 3019 cm^{-1}. In the same way, 0.74 eV energy must be given at a frequency of the same wave number to overtone the v_3 vibration mode. This study discusses the initiation or acceleration of reactions with lower activation energies because of inelastic collisions of a vibrationally excited CH_4 molecule with hydrogen with a specific kinetic energy. In addition, the breaking of chemical bonds resulting from the collision and the formation of new bonds were evaluated theoretically.

Since the v_3 vibrational mode energy of the CH_4 molecule and the v_1 vibrational mode energies for the methyl group (CH_3) are very similar, the scattering dynamics as a result of the reaction may cause a similar result to be produced.

As a result, research for the development of simplified models of molecules containing more than four atoms is presented in this study. Theoretical studies have revealed that C—H stretch excitation increases the reaction rate of hydrogen and methane to CH_4.

It is thought that these reactions may be sufficient to initiate chain reactions. It has been shown that as a result of the reaction of the v_3 vibrational excited CH_4 molecule with hydrogen, the v_1 vibrational mode excited CH_3 molecule can be formed. It is understood that with the excitation of the CH_3 molecule, the reaction of hydrogen abstraction from this molecule can be accelerated and facilitated.

In addition, it has been demonstrated that asymmetric stretching modes in methane can be achieved by absorption with electromagnetic radiation at wavelengths of 1.7 μm and 3.3 μm in the infrared region. The energy of 0.37 eV (36.12 kJ/mol) or 0.74 eV (72.24 kJ/mol) is required to generate electromagnetic radiation in this IR region. When the proposed method is validated experimentally, solar energy can achieve UV photolysis naturally. In conventional methods, 439.3 kJ/mol needs to break the H-CH_3 bond. This value is tried to be lowered with the help of various catalysts. It is also envisaged that these reactions will be carried out at lower temperatures. In these respects, this method has many advantages.

In future studies, hydrogen abstraction reactions from CH_3, CH_2 and CH molecules can be examined similarly and all possible reactions can be determined. Also, reaction rates and equilibrium constants for all reactions can be determined.

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