

Photodissociation of Methane at Lyman Alpha (121.6 nm)

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Laser induced fluorescence studies of hydrogen atom using four wave mixing technique are reported for the photodissociation of CH₄ and its isotopomers at Ly α (121.6 nm). The source of dissociating and probe radiation is one and the same (delay time \leq 20 nsec). The average translational energy of ejected hydrogen atoms (50 Kcal/mol) reveals that CH₄ + $h\nu$ \rightarrow CH₃ + H(²S) and CH₄ + $h\nu$ \rightarrow CH₂(a¹A₁) + H₂(¹ Σ _g) are the main dissociation processes. The absolute quantum yield for CH₄ and CD₄ are the same, $\Phi_{\text{H}}(\text{CH}_4) = \Phi_{\text{D}}(\text{CD}_4) = 0.31 \pm 0.05$. If one divides the experimental H/D ratios from the isotopomers CH₃D, CH₂D₂, CHD₃ by the isotopic H/D ratios, a value 2 is obtained in all three cases. Overall, the heavier D atoms are more likely than the H atoms to remain attached to the carbon atom.

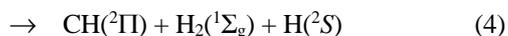
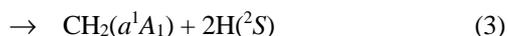
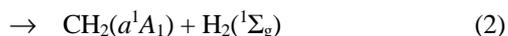
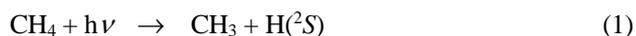
Key Words : Photodissociation, Methane, Lyman α , LIF, Quantum yield

Introduction

The photochemistry of methane has been the subject of numerous investigations¹ not only for its intrinsic chemical importance but also for the implications relating to other branches of science. Methane is the most abundant hydrocarbon on earth and is present in small amounts in the atmospheres of all the planets. For example, in the atmosphere of Jupiter its mole fraction is about 2×10^{-3} .² The most remarkable exception is the atmosphere of Titan, a moon of Saturn which has 2%–3% methane. In order to construct a photochemical model for this atmosphere, it is essential to know the yields of the different photodissociation channels at 121.6 nm (Ly α).

In order to model photodissociative processes of methane, the single most important wavelength for which data is required is 121.6 nm, the Ly α line. This is because of its great relative intensity, as shown by the fact that the Ly α flux is equal to that for all other solar radiation between 120 and 160 nm.³ Under conditions where an absorbing molecule has a high cross section at Ly α and only absorbs weakly, if at all, beyond 170 nm, photodissociative data at Ly α become essential.

The past few years have witnessed renewed interest in experimental studies of the photodissociation of CH₄, particularly at Ly α photon energy.^{4–9} Four important dissociation channels have been found:



Slanger and Black⁴ used resonance fluorescence to monitor the total H atom yield arising from Ly α dissociation of CH₄, and estimated a quantum yield for forming H atoms: $\Phi_{\text{H}} = 1.16$. Mordaunt *et al.*⁵ pointed out the significance of H-atom elimination in this process, and estimated $\Phi_{\text{H}} = 1.0 \pm$

0.5. The use of H atom Rydberg time-of-flight technique also allowed them to conclude that a very significant part of the H atom fragments is formed concomitant with methyl radicals. From their works and observations by Heck *et al.*⁶ using photofragment imaging technique, it was revealed that a slower H atom channel can arise from the sequential decomposition of the internally excited methyl fragments or from the concerted triple-fragment decay processes. Using the Ly α photolysis of H₂O as a reference, Brownsword *et al.*⁷ were able to establish the absolute quantum yield for the H atom formation for CH₄ at Ly α , $\Phi_{\text{H}} = 0.47 \pm 0.11$. More recently, Wang *et al.*⁹ reported a complete set of quantum yields for the different photodissociation channels of methane and its isotopomers. Comparing quantum yields from several research groups, the values were a little different. Each research group was using somewhat different ‘pump-probe’ techniques and different reference sources to evaluate quantum yield of methane.

In this work we report the average kinetic energy of ejected hydrogen atoms, the absolute quantum yields of each dissociation channel, and H/D ratios for the photodissociation of CH₄ and its isotopomers at 121.6 nm. Four wave mixing technique was used to generate intense Ly α and HCN was chosen as a reference molecule to determine the absolute quantum yield.

Experimental Section

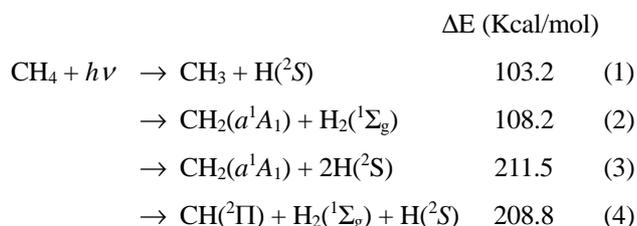
To generate intense Ly α , the four wave mixing technique¹⁰ was used. This work was achieved by using an intermediate resonance with the 5P[1/2]_o state of Kr at 94093 cm⁻¹, a $2\omega_1 - \omega_2$ process in which ω_1 was fixed at 47046.5 cm⁻¹ and ω_2 was in the 845 nm region. We used only one wavelength to dissociate methane and to detect hydrogen atoms. In other words, the first photon of Ly α light dissociated parent molecules into radicals and hydrogen atoms, and the second photon was used to detect hydrogen atoms by laser induced fluorescence (LIF). Therefore, the width of the

dye laser pulse (~20 nsec) was almost the maximum delay time between exciting and probing light because both photons originate from same pulse.

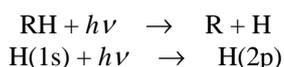
Methane molecules were photodissociated and detected in a vacuum cell by Ly α at a pressure of 20-150 mT. The H atom VUV fluorescence was focused onto a solar blind photomultiplier tube (EMR 542 G-08-17) which was oriented perpendicular to the original light. The H atom fluorescence intensity (A channel) and original Ly α flux intensity (B channel) were simultaneously monitored by two solar blind multipliers. The A/B signal was collected with a boxcar averager (Stanford Research System Model SR250) and sent to a computer for analysis.

Results

The photon energy at 121.6 nm is 10.2 eV (235.1 Kcal/mol), and available spin-allowed channels for CH₄ photodissociation are:



In this work, we measure LIF signal of hydrogen atoms produced by Ly α photodissociation of methane. The source of the dissociating radiation and the source of the probe radiation are one and the same. In other words two processes occur during the approximately 20 ns width of the laser pulse:



Here RH is the methane molecule and $h\nu$ is the Ly α photon. By sweeping the laser through the absorption of the hydrogen atom the shape of the fluorescence excitation curve is measured; in turn, the average kinetic energy can be calculated from the equation¹¹

$$\langle E_T \rangle = m \langle v^2 \rangle / 2 = mc^2 \langle v - v_0 \rangle^2 / 2v_0^2$$

where v_0 is the absorption frequency of a H atom at rest and v is the absorption frequency of the H atom with velocity v .

In our experiment, the average translational energy of the hydrogen atom ejected from excited methane is ~50 Kcal/mol (Table 1). Process (3) and (4), therefore, seem to be not important processes in this wavelength (121.6 nm). It is concluded, therefore, that the main processes for the photodissociation of methane at $\lambda = 121.6$ nm are (1) and (2).

Table 1 shows the average translational energies and a number of H/D ratios of atoms ejected from excited deuterated methane series at $\lambda = 121.6$ nm. All the kinetic energies of H and D atoms are around 50 Kcal/mol and the statistical H/D ratio per atom is around 2. These ratios are, in essence, the ratios of rate constants for generating hydrogen

Table 1. Average kinetic energy of the H atom, H/D ratios, absorption coefficients, and absolute quantum yields of methane

Molecule	$\langle E_T \rangle$ (Kcal/mol)	H/D	k ($\text{atm}^{-1}\text{cm}^{-1}$)	Absolute quantum yields
CH ₄	49.5 ± 4.9		485 ^a	0.31 ± 0.05
CH ₃ D	50.1 ± 4.7 (H) 41.9 ± 8.2 (D)	5.89 ± 0.58		
CH ₂ D ₂	51.4 ± 3.0 (H) 52.7 ± 10.1 (D)	1.99 ± 0.18		
CHD ₃	48.7 ± 8.4 (H) 51.9 ± 6.0 (D)	0.63 ± 0.06		
CD ₄	55.0 ± 6.7		485 ^b 587 ^c	0.31 ± 0.05 0.26 ± 0.04
1:1 CH ₄ /CD ₄		1.01 ± 0.13		
HCN			672 ^d	(1)

^aref. 23. ^bSee the text. ^cref. 12. ^dref. 24.

atoms. These results show that H atoms come out more easily than the D atoms from the excited molecule. Figure 1 represents the LIF spectra of H and D atoms from the photodissociation of CH₃D, CH₂D₂, and CHD₃, respectively.

To measure quantum yields for several processes, the ratio of the LIF signal of hydrogen atoms from one species (HR) to that from the other species (HR') was measured. The

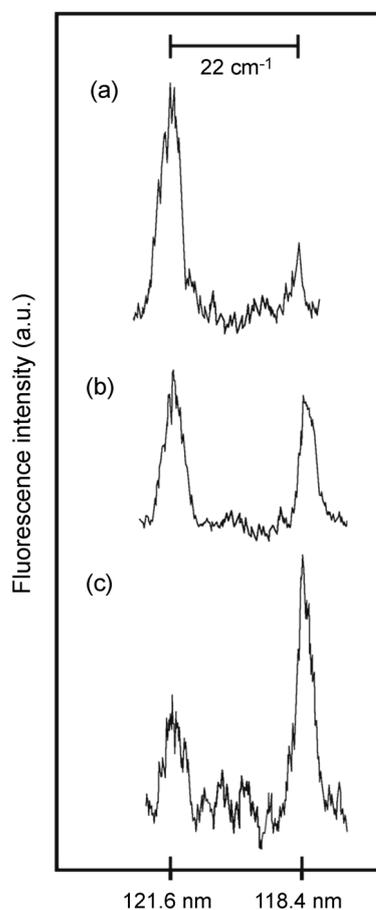


Figure 1. Laser induced fluorescence signal of H and D atoms for (a) CH₃D, (b) CH₂D₂, and (c) CHD₃.

following equation was then used for calculation;

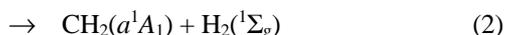
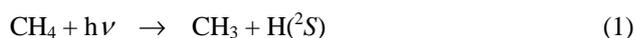
$$\frac{A_H(\text{HR})}{A_H(\text{HR}')} = \frac{\varepsilon_{\text{HR}} P_{\text{HR}} \Phi_H(\text{HR})}{\varepsilon_{\text{HR}'} P_{\text{HR}'} \Phi_H(\text{HR}')}$$

where ε_i , A_i , and P_i are the molar absorption coefficient, the area under the fluorescence curve, and pressure of species i . Absorption coefficients at Ly α listed in Table 1 were obtained from several references.

To determine the absolute quantum yield, HCN was chosen as a reference molecule. As it is impossible to break the CN bond in HCN by Ly α light the dissociative channels would always produce H atoms with unit quantum yield. The absolute quantum yield $\Phi_H(\text{CH}_4)$ or $\Phi_D(\text{CD}_4)$ was obtained directly by comparison with the HCN photodissociation by introducing those molecules alternatively to the experimental chamber. The quantum yields for CH_4 and CD_4 were obtained to be $\Phi_H(\text{CH}_4) = 0.31 \pm 0.05$, and $\Phi_D(\text{CD}_4) = 0.26 \pm 0.04$, respectively, with the absorption cross section values in Table 1. Some time ago, somewhat coarse-grained spectra of CH_4 and CD_4 were reported which showed that at 10.2 eV CD_4 absorbed about 20% more strongly than CH_4 .¹² Wang *et al.*⁹ have measured the spectra of CH_3D and found that the spectrum is almost identical in shape and strength to that of CH_4 . When we used the same absorption cross section for CH_4 and CD_4 as $485 \text{ atm}^{-1}\text{cm}^{-1}$ to calculate the quantum yield, the final values for CH_4 and CD_4 were obtained to be same, *i.e.* $\Phi_H(\text{CH}_4) = \Phi_D(\text{CD}_4) = 0.31 \pm 0.05$ within experimental error.

Discussion

We concluded that the main processes for the photodissociation of methane at $\lambda = 121.6 \text{ nm}$ are only (1) and (2) since $\langle E_T \rangle$ of hydrogen atoms ($\sim 50 \text{ Kcal/mol}$) plus the enthalpy of formation is less than 235.1 Kcal/mol (121.6 nm):

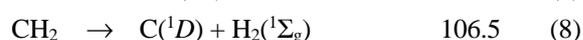


If $\langle f_T \rangle$ is defined as the fraction of the total energy available to the $\text{CH}_3 + \text{H}$ dissociation channel that is partitioned into product translation, the calculated $\langle f_T \rangle$ is ~ 0.30 by using the following formula, $\langle f_T \rangle = \langle E_T \rangle / (E(\text{photon}) - \text{bond energy})$. This value is quite low with respect to direct dissociation.¹³ Mordaunt *et al.*⁵ also found CH_3 fragments with very high levels of internal excitation. And they suggested that CH_4 molecules prepared in their triplet (S_1) A excited state undergo rapid internal conversion to higher vibrational levels of the ground state before dissociation.

Because the quantum yield of process (1) is around 0.31 the quantum yield of process (2) should be around 0.69. The yield for H_2 elimination at 123.6 nm has been measured by Laufer and McNesby¹² as 0.58 and the H atom yield alone was reported by Slanger and Black⁴ as 1.14. These inconsistencies with our results seem to be attributed to different experimental conditions. As we explained in Experimental Section, only one wavelength ($\lambda = 121.6 \text{ nm}$) was used to

dissociate methane and to detect hydrogen atoms. Therefore the maximum delay time between exciting and probing light is same as the width of dye laser pulse ($\sim 20 \text{ nsec}$) itself. In other words, we detected the nascent H atom within a 20 nsec delay time after firing the exciting laser. However, other groups used a much longer delay time ($\geq 50 \text{ ms}$) or used a mass spectrometer to analyze products by cooling the reaction mixture with liquid hydrogen. Thus they detected all the final products from secondary reactions, which could not be detected in our system, as well as primary reactions (1) and (2).

The possible secondary reactions are:

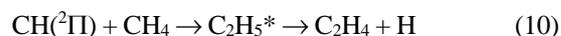
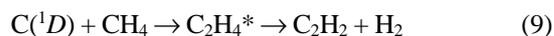


The maximum internal energy, E_{int} , which a CH_3 or CH_2 radical has can be calculated from the following formulae:

$$E_{\text{int}}(\text{CH}_3) = \text{photon energy} - \Delta E \text{ of primary reaction (1)} - E_T(\text{H})$$

$$E_{\text{int}}(\text{CH}_2) = \text{photon energy} - \Delta E \text{ of primary reaction (2)}$$

The calculated values are $E_{\text{int}}(\text{CH}_3) = 82.3 \text{ Kcal/mol}$ and $E_{\text{int}}(\text{CH}_2) = 126.8 \text{ Kcal/mol}$. Therefore, (5) and (6) are energetically unfavorable processes and only (7) and (8) are available. The formation of CH radicals and C atoms in the photolysis of methane has been reported by a number of investigators.¹⁵⁻¹⁸ The quantum yields have also been obtained¹⁸ for the formation of $\text{C}(^1D)$ and $\text{CH}(^2\Pi)$ species at 123.6 nm ($\Phi(\text{C}) = (0.4 \pm 0.1) \times 10^{-3}$, $\Phi(\text{CH}) = (5.9 \pm 0.5) \times 10^{-2}$). If these numbers are correct, the absolute quantum yield for the formation of $^1\text{CH}_2$ would be lowered to 0.63 from 0.69. In these experiments $\text{C}(^1D)$ and $\text{CH}(^2\Pi)$ were detected through the products of their fast reaction with CH_4 .¹⁸⁻²⁰



In the above reactions (9) and (10), $\text{CH}(^2\Pi)$ and $\text{C}(^1D)$ seem to mainly originate from the secondary processes (7) and (8) because processes (5) and (6) are not available energetically as discussed previously. In other words, CH and C may result from dissociation of CH_2 instead of CH_3 as precursor. The H atom yield, 1.14, which Slanger and Black found, is actually the summation of processes (1), (3), (4), (7), and (10). Conclusively, the absolute quantum yields for the process (1) and (2) in this system, 0.31 and 0.63, are in excellent agreements with the results from ref 9, 0.29 and 0.59. The main difference between two research groups was to use different reference molecule, *i.e.* HCN and H_2O to determine absolute quantum yield. The absolute quantum yield in this work was based on assumption of $\Phi_H(\text{HCN}) = 1$ as used in other Ly α experiments.^{5,21} As it is impossible to break the CN bond in HCN by Ly α light the dissociative channels would always produce H atoms with unit quantum

yield.

The H/D isotopic ratios listed in Table 1 for the series of partially deuterated methanes show that the H atom is always the preferential photofragment. In fact, if one divides the experimental H/D ratio by the isotopic H/D ratio in the parent molecule, a value 2 is obtained in all three cases. An even stronger isotope effect was found for HDO at 157 nm²² and the explanation is probably similar. The vibrational wave function of the lighter atom could be more diffuse and extends further into the strongly repulsive region. One might assume that with a photon of 235 Kcal/mol being absorbed by the molecule all directions would be repulsive. However, speaking classically, the initial motion might be along the symmetric stretch coordinate which can lead to dissociation only if there is enough energy in the molecule to break all four bonds at once, an impossibility at this energy. In the subsequent more complex motion the lighter isotope is more apt to be found on the outward going part of the potential surface.

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