

Modeling of methane photolysis in the reducing atmospheres of the outer solar system

Nicholas S. Smith and François Raulin

Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université Paris 12, Val de Marne
Créteil, France

Abstract. It is important that methane photolysis is accurately treated in models of planetary atmospheres of the outer solar system and of the interstellar medium. Recent measurements of the H atom and H₂ yields in the photolysis of methane have been considered and appear to be consistent with quantum yields, at Lyman α (121.6 nm), of (R1) CH₃ + H = 0.41, (R2) ¹CH₂ + H₂ = 0.53, (R3) ¹CH₂ + H + H = 0.0, (R4) ³CH₂ + H + H = 0.0, and (R5) CH + H₂ + H = 0.06. At shorter wavelengths it is likely that the production of CH will increase due to the decomposition of excited CH₃ molecules, although further data are required to be able to accurately model the wavelength dependence of methane photolysis. At the low temperatures of Titan's atmosphere, for example, the possible temperature dependence of CH₄ absorption cross sections may need to be considered. By reference to other hydrocarbons, the absorption of methane may increase by 30% or more at 200 K with respect to room temperature values. These dependences, not previously considered in photochemical models of Titan, could significantly change the predicted composition of Titan's atmosphere and the chemical pathways implied.

1. Introduction

Methane, the simplest of hydrocarbons, is an important trace constituent of Earth's atmosphere. It is also a major reactive component in the atmospheres of many other objects in the outer solar system, notably Titan, the largest moon of Saturn. As CH₄ only absorbs ultraviolet radiation short of 145 nm [Mordaunt *et al.*, 1993], its photolysis is dominated by Lyman α radiation at 121.6 nm.

In order to model the photochemistry of methane accurately, we need precise values for the absorption cross sections and quantum yields for the primary dissociations. Analyses of product yields after irradiation, using Kr or Ar emission lines [Ausloos *et al.*, 1964; Gorden and Ausloos, 1967], have been difficult to interpret because of the complexity of possible secondary reactions. However, more recent direct measurements, using photofragment imaging techniques [Heck *et al.*, 1996; Mordaunt *et al.*, 1993], have given us a clearer picture of the primary photodissociation mechanisms. The question that now needs to be addressed is whether these results can be combined to give a coherent picture of the photolysis of methane and how much confidence the modeler can place in these values. This is particularly important in the case of Titan, where methane is a major constituent of the atmosphere. So far, the photochemical models of Titan do not provide a quantitative explanation of all observational data [Gautier, 1997; Lara *et al.*, 1996; Toublanc *et al.*, 1995; Yung *et al.*, 1984].

2. Absorption Cross Sections

Measurements, at room temperature, of methane cross sections seem to be in good agreement [Lee and Chiang, 1983; Mount *et al.*, 1977; Watanabe *et al.*, 1953]. Absorption observed at wavelengths longer than 145 nm [Mount and Moos, 1978; Mount *et al.*, 1977] can be attributed to the presence of impurities in the methane sample. The absorption appears continuous and has a value of approximately 2×10^{-17} cm² between 110 and 130 nm. Can we, however, use these data when modeling cold environments, such as planetary atmospheres in the outer solar system or the interstellar medium?

It appears that the only measurement of CH₄ cross sections at low temperature (200 K) was carried out over the narrow wavelength range of 138–147 nm [Mount and Moos, 1978; Mount *et al.*, 1977]. A decrease in absorption of approximately 20% was noted at the longest wavelengths and was explained as a depopulation of excited vibrational states. We could therefore reasonably expect an increase in absorption at shorter wavelengths due to increased population of lower energy vibrational states. Because of its large intensity in the solar spectrum, the principal wavelength for methane photolysis in planetary atmospheres is Lyman α , 121.6 nm. As no data exist at low temperatures for this wavelength, we need to estimate the possible increase in absorption cross section.

Recent studies of a large number of unsaturated hydrocarbons, such as C₂H₂ [Chen *et al.*, 1991; Wu *et al.*, 1989], CH₃C₂H [Fahr and Nayak, 1996], C₃H₆ [Fahr and Nayak, 1996], C₄H₂ [Fahr and Nayak, 1994], and C₆H₂ [Bénilan *et al.*, 1995], have shown that the variation of mid-ultraviolet absorption cross sections as a function of temperature can be important. Although these studies were carried out longward of 160 nm, some bands arising from

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Rydberg transitions were studied over the temperature range of 220-300 K [Fahr and Nayak, 1996, 1994]. The intensity of the 164.6 nm Rydberg band of C_4H_2 increases by 30% at low temperature, although this behavior may have been affected by the presence of an impurity, namely, C_4H_3Cl [Smith *et al.*, 1998]. However, the 40% increase of the Rydberg bands of C_4H_4 (163.8 nm and 168.2 nm) and the 80% increase of the 186.6 nm Rydberg band of C_4H_6 give strong evidence that the temperature dependence of band intensities is important for Rydberg transitions. As methane absorption in the range 110-130 nm has been attributed to a number of Rydberg transitions [Lee and Chiang, 1983], we could perhaps expect an increase of 30%, or more, in the absorption cross sections of CH_4 when we consider temperatures as low as in Titan's atmosphere ($T < 200$ K). Clearly, it is imperative that methane's absorption coefficients be measured at low temperatures, at least at the Lyman α wavelength, but preferably over the whole range of absorption. Not only could a variation in these coefficients affect the results of photochemical models of Titan, they would also influence associated radiative transfer calculations, as methane is the major absorbing species at the Lyman α wavelength.

3. Primary Quantum Yields

Determination of the primary quantum yields in methane photolysis has not been straightforward, due to the difficulty of detecting the CH_x fragments. There are five branches that are energetically accessible at 121.6 nm ;

- | | | |
|------|------------------|-------------------------|
| (R1) | $CH_3 + H$ | $\lambda \leq 276.6$ nm |
| (R2) | $^1CH_2 + H_2$ | $\lambda \leq 247.3$ nm |
| (R3) | $^1CH_2 + H + H$ | $\lambda \leq 130.7$ nm |
| (R4) | $^3CH_2 + H + H$ | $\lambda \leq 134.5$ nm |
| (R5) | $CH + H_2 + H$ | $\lambda \leq 136.6$ nm |

By analyzing the production yield of certain species, the relative importance of branches (R1)-(R5) can be estimated.

3.1. H Atom Yield

Photofragment imaging of H atoms has demonstrated the importance of process (R1). Hydrogen atoms with large amounts of kinetic energy can only be formed with methyl fragments, and these "fast" H atoms make up about 87% of the total H atom yield [Heck *et al.*, 1996]. The remaining 13% is the sum of processes (R3), (R4), and (R5), although the exact nature has not yet been determined.

The quantum yield of H atom production from CH_4 ($QY_H(CH_4)$) has been measured relative to the quantum yield of H production from H_2O . Initially, a greater H atom yield was determined for CH_4 than for H_2O [Slanger and Black, 1982], but it appears that this experiment suffered from secondary photolyses of hydrocarbon fragments and previously formed products. The H yield for methane has been recently remeasured and now appears to be about half that of H_2O [Brownsword *et al.*, 1997b].

The absolute H atom quantum yield of H_2O ($QY_H(H_2O)$) was quantified by measuring the production of H and $O(^3P)$ atoms by resonance fluorescence [Slanger and Black, 1982]. Three channels were determined :

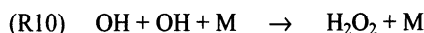
- | | |
|------|-------------------------|
| (R6) | $OH + H = 78\%$ |
| (R7) | $O(^1D) + H_2 = 10\%$ |
| (R8) | $O(^3P) + H + H = 12\%$ |

This gives a value of $QY_H(H_2O) = 1.02$. The quantum yield of 0.1 for process (R7) was in good agreement with a previous study [Stief *et al.*, 1975]. The quantum yield for process (R8) was determined relative to process (R7), by measuring the $O(^3P)$ yield with and without the presence of an excess of N_2 , which deactivates all $O(^1D)$ to $O(^3P)$.

The apparent 12% contribution from process (R8) must, however, be considered with caution. The authors note that a concentration of OH radicals higher than $3 \times 10^{10} \text{ cm}^{-3}$ would lead to significant production of $O(^3P)$ atoms through the recombination of OH with itself :



Unfortunately, it appears that the intensity of the hydrogen lamp used was not determined. Typically, a hydrogen lamp of this type has a flux of 10^{14} - 10^{15} photons/s. If the flux were toward the upper end of this range, the OH concentrations could have been as high as 10^{11} cm^{-3} . Any formation of H_2O_2 , by the recombination of OH with itself



may have increased the effective concentration of OH due to its subsequent photolytic decomposition back to two OH radicals. Thus process (R9) could possibly explain the observed concentrations of $O(^3P)$ atoms and the quantum yields for photolysis of H_2O are in the ranges (R6) = 0.9-0.78, (R7) = 0.1, and (R8) = 0-0.12. This results in a reassessed value of $QY_H(H_2O)$ that is in the range 0.9-1.02.

The latest measurement of the relative yield of H atoms from methane [Brownsword *et al.*, 1997b] found, from Doppler profiles, is

$$QY_H(CH_4) = 0.46 \times QY_H(H_2O)$$

The authors used the previously determined $QY_H(H_2O) = 1.02$, and considering a 20% error in this value, calculated $QY_H(CH_4) = (0.47 \pm 0.11)$. If we consider that the value of $QY_H(H_2O)$ has more likely been overestimated than underestimated, we could expect the value of 0.47 to be near the possible maximum value for $QY_H(CH_4)$. As we shall see below, a value of $QY_H(CH_4) \leq 0.5$ argues against a significant role for three-body dissociations of methane.

3.2. H_2 Yield

Photofragment imaging of H_2 molecules, eliminated after absorption of two ultraviolet photons (210-230 nm), has shown the presence of two separate formation pathways [Heck *et al.*, 1996]. Fast H_2 molecules, from energetic arguments, must be formed from process (R2) in conjunction with 1CH_2 . As a $^3CH_2 + H_2$ channel is spin-forbidden, the remaining "slow" H_2 must be formed in a three-body dissociation such as process (R5). Fast H_2 appears to be formed with large amounts of internal energy, and there is significant population of higher vibrational energy levels. An analysis by vibrational level shows processes (R2) and (R5) to have equal importance for $v=1$, but (R2) dominates at higher vibrational levels. To be able to fully quantify the ratio of process

(R2) to process (R5), a full analysis of all H₂ vibrational levels would be necessary. However, it appears as though (R2) is the dominant pathway and accounts for at least two thirds of the total H₂ yield.

The absolute quantum yield for H₂ production has been measured from the simultaneous photolysis of CH₄ and CD₄ with and without radical scavengers [Laufer and McNesby, 1968]. With a scavenger, such as C₂H₄, present, the yield of H₂ ($\Phi(\text{H}_2, \text{M})$) corresponds to that which is formed from molecular elimination. Without a scavenger, the H₂ yield ($\Phi(\text{H}_2, \text{T})$) is the sum of the molecular elimination and the secondary reactions of H atoms which give rise to H₂. It was found that

$$\Phi(\text{H}_2, \text{M}) / \Phi(\text{H}_2, \text{T}) = 0.74$$

By comparison with the quantum yields of CO production from CO₂, $\Phi(\text{H}_2, \text{T}) = 0.8$. This results in a "molecular" hydrogen quantum yield, $\Phi(\text{H}_2, \text{M}) = 0.59$. Studies performed in the presence of an excess of argon gas show that $\Phi(\text{H}_2, \text{T})$ from CH₄ decreases by 13%, while $\Phi(\text{D}_2, \text{T})$ from CD₄ is unaffected. This suggests the production of some H₂ from a secondary fragmentation process.

3.3. CH_x Fragment Yields

In general, CH_x fragment yields have been difficult to determine accurately, although certain excited species have been detected by fluorescence techniques. Methylene radicals appear to be predominately formed in the ground singlet (¹A₁) state, although fluorescence of the (¹B₁) state has been observed [Lee and Chiang, 1983]. The yield of CH₂ (¹B₁) is very minor but appears to increase with decreasing wavelength, reaching a maximum of 1.5% of the total CH₂ production at 106 nm.

CH radicals have also been monitored spectroscopically in the flash photolysis of methane [Braun et al., 1967]. It appears that the yield of CH radicals is considerably larger than in the low-intensity photolysis. This can be explained by secondary photolysis of CH₃ and / or CH₂ radicals under the high-intensity conditions of the flash. The low-intensity production of CH appears to depend strongly on the wavelength of photolysis, becoming more important at shorter wavelengths. At 123.6 nm, QY(CH) = 0.06, while at 104.8-106.7 nm, QY(CH) = 0.23 [Rebbert and Ausloos, 1972/73]. There may also be a very small production of C(¹D) atoms, which may be due to photolysis or decomposition of CH or CH₂ radicals.

4. Discussion

In summary, if we consider the low-intensity photolysis of CH₄ to be similar at 121.6 nm and 123.6 nm, the quantum yields that have been determined are

$$\text{QY}(\text{H}) = 0.47$$

$$\text{QY}(\text{H}_2) = 0.59$$

$$\text{QY}(\text{CH}) = 0.06$$

The combined yield of H and H₂ is 1.06, so three-body decompositions are fairly minor. The value of QY(CH) suggests that all three-body decompositions lead to CH. If we assume this to be true we can calculate primary quantum yields of

$$(R1) \quad \text{CH}_3 + \text{H} = 0.41$$

$$(R2) \quad {}^1\text{CH}_2 + \text{H}_2 = 0.53$$

$$(R3) \quad {}^1\text{CH}_2 + \text{H} + \text{H} = 0.0$$

$$(R4) \quad {}^3\text{CH}_2 + \text{H} + \text{H} = 0.0$$

$$(R5) \quad \text{CH} + \text{H}_2 + \text{H} = 0.06$$

This agrees with the observation that 87% of H atoms are formed concomitant with CH₃ radicals. It also supports the idea that simple C-H bond fission is an important primary process [Mordaunt et al., 1993]. The methylene can be considered almost entirely as CH₂ (¹A₁).

It has been proposed that some of the CH₃ radicals are formed with enough excess energy to further decompose [Mordaunt et al., 1993]. Lyman α photons supply 10.2 eV to the methane molecule, of which only 4.5 eV is required to break the C-H bond. This leaves 5.7 eV of excess energy, which corresponds well with the maximum H atom velocities measured (32 km/s). Methyl radicals formed with more than 4.7 eV of excess energy are able to decay into CH + H₂, or with a little more energy, into ³CH₂ + H. It appears that many of the methyl radicals formed are close to this dissociation limit [Heck et al., 1996] and thus the production of CH may be entirely due to decomposition of excited CH₃. If this were the case, we would expect the quantum yield for CH to diminish to zero at high pressures. It has been observed that the presence of a large excess of argon in the photolysis of methane reduces the quantum yield of H₂ formed by 13% [Laufer and McNesby, 1968], and this agrees well with the suppression of process (R5) at high pressure. However, experimental data show that the observed 13% decrease in H₂ yield was most probably due to the presence of the reaction CH + H₂ + M \rightarrow CH₃ + M, important only at high total pressures [Brownsword et al., 1997a; Fulle and Hippler, 1997].

It is reasonable therefore to expect a proportion of CH to be formed in primary process (R5), while some is formed from decomposition of excited CH₃. This latter channel may go some way to explaining the large increase in the QY(CH) at shorter wavelengths, as extra energy is deposited into the CH₃ fragment and hence a larger proportion decomposes. There is also the possibility that some excited CH₃ decomposes to ³CH₂ + H. To fully understand the formation of CH and the possible formation of excited CH₃, photofragment imaging experiments need to be performed for a range of photolysis wavelengths, to investigate the variation in fast and slow H and H₂ fragments formed.

5. Conclusions

The primary quantum yields of methane photodissociation

$$(R1) \quad \text{CH}_3 + \text{H} = 0.41$$

$$(R2) \quad {}^1\text{CH}_2 + \text{H}_2 = 0.53$$

$$(R3) \quad {}^1\text{CH}_2 + \text{H} + \text{H} = 0.0$$

$$(R4) \quad {}^3\text{CH}_2 + \text{H} + \text{H} = 0.0$$

$$(R5) \quad \text{CH} + \text{H}_2 + \text{H} = 0.06$$

appear to be consistent with the observations, to date, of methane photolysis at, or close to, the Lyman α wavelength (121.6 nm). It is still unclear whether CH is formed in a direct three-body process or is the result of stepwise decomposition of CH₃ fragments formed with large amounts of internal energy. Studies at shorter wavelengths should help clarify this. Equally important for photochemical modeling is the determination of the absorption

cross sections of methane at low temperature, as they may be as much as 30% higher than the room-temperature values currently used.

To date, the sensitivity of photochemical models of Titan's atmosphere has not been systematically investigated. A variation in CH₄ absorption at low temperature will change the total destruction rate of CH₄. It is also highly likely that changes in the primary quantum yields of CH₄ photolysis will induce a notable variation in the model. As the values calculated above differ markedly from the values used in previous models, there is clearly a need to perform sensitivity studies for these quantum yields. Such modeling studies are currently under way to quantify the influence of methane photolysis in Titan's atmosphere.

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F. Raulin and N.S. Smith, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Université Paris 12 Val de Marne, 61, Avenue du Général de Gaulle, 94010 Créteil Cedex, France. (raulin@lisa.univ-paris12.fr; smith@lisa.univ-paris12.fr)

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