Reactivity of methane in a nitrogen discharge afterglow

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Abstract. This work is devoted to the study of the reactivity of CH₄ in a nitrogen afterglow. We show that CH₄ reacts efficiently in the nitrogen afterglow producing the simple radicals CH₃, CH₂ or recombined species containing C–N bonds in the form of C₂N₂, CN or HCN. A reaction rate constant ranging between 1 × 10⁻¹⁸ and 6 × 10⁻¹⁸ m³ s⁻¹ is found for the global reaction producing mainly CH₂ and CH₃ radicals. Investigations are also performed in order to determine which ‘active’ nitrogen species are involved in the dissociation mechanism of CH₄ in the nitrogen afterglow. To do this we study elementary reactive processes between CH₄ and specific nitrogen species such as N₂(A³Σ⁺,v), and N atoms. N₂(A³Σ⁺,v) is selectively produced by energy transfer from Ar(⁴P₂) metastable species to N₂, before reacting with CH₄. We show that this reaction is efficient and leads mainly to the formation of CH₃ and C₂H₆. According to the literature, the higher the vibrational level is the faster is the rate of the vibrational relaxation of N₂(A³Σ⁺,v). We also study the reaction of CH₄ with N atoms in the nitrogen afterglow. We measure a reaction rate constant ranging between 2 × 10⁻¹⁸ and 6 × 10⁻¹⁸ m³ s⁻¹. This value is larger than the value reported elsewhere in the literature and close to the value given for the reaction of CHₓ<4 with N atoms. So we propose the following reaction mechanism for the dissociation of CH₄ in a nitrogen afterglow. First CH₄ reacts with vibrationally excited metastable species N₂(A³Σ⁺,v) coming from the nitrogen discharge that produces CHₓ<4 simple radicals. Then these radicals react with N atoms producing hydrogen cyanide, cyanogen and hydrocarbons.

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1. Introduction

Plasma discharges produced in methane, nitrogen or methane–nitrogen gas mixtures are widely used in various technical applications, for example in catalysis [1], combustion [2, 3], conversion of methane [4] or surface treatments [5].

The understanding and the modelling of the complex chemical system implicated in plasma discharge require a complete knowledge of different elementary reaction processes and reaction rate constant values. Many studies have already been performed regarding nitrogen discharge [2, 3, 6] or methane–nitrogen discharge [7, 8]. There is a growing interest in the use of flowing nitrogen afterglow in order to study ‘active’ nitrogen species in the field of energy transfer with other species [6, 9, 10].

This work is devoted to the study of the reaction of methane in a nitrogen microwave discharge afterglow. We study the methane dissociation mechanism in a nitrogen afterglow and we measure the total dissociation rate constant of the reaction producing CH$_2$ and CH$_3$ radicals. Then we compare this value to other dissociation rate constant values reported elsewhere or measured in this work for various elementary processes in order to determine which ‘active’ nitrogen species are involved in the methane conversion in nitrogen discharges.

2. Experimental set-up

The experimental set-up is schematically shown in figure 1. It consists of a nitrogen microwave discharge produced in a quartz tube (outer diameter 19 mm and inner diameter 16 mm) used as a nitrogen source. A microwave discharge working at 2.45 GHz is produced by means of a SAIREM GMP 12 KE generator within the wave launcher connected to a flowing afterglow stainless steel tube. In order to maintain a constant wall temperature, the outside of the quartz tube is refreshed by means of air-cooling. The total pressure is maintained constant at 40 Pa using a Roots blower pump operating at 70–700 m$^3$ h$^{-1}$.

The optical diagnostic is carried out using a high-resolution spectrometer (Jobin Yvon THR 1000 resolving power 100 000 at 500 nm), equipped with a photomultiplier tube (Hamamatsu R928). Observations are performed close to the exit of the methane injector (205 mm above the discharge centre) and 195 mm upstream of the mass spectrometer sample hole). The optical signal is introduced into the entrance slits of the spectrometer using an optical fibre (PCS 600) collecting the signal focused by a 200 mm focal lens.

Analysis is performed by means of a quadrupole mass spectrometer (QMG 421 Balzers) equipped with a secondary electron multiplier amplifier. The gas is sampled through a 50 $\mu$m diameter hole 400 mm downstream of the discharge centre (i.e. 195 mm above the methane injector exit).

The methane is injected downstream of the nitrogen discharge (200 mm above the microwave launcher centre). The main species detected in the afterglow by means of a mass spectrometer placed 400 mm above the discharge centre are shown in table 1. The nitrogen discharge is working at 40 Pa and 100 W and the methane flow injected is equal to 5 sccm. The electron energy is kept constant and equal to 13.5 eV. This value is larger than the ionization threshold of the main species produced. Nevertheless it stays low enough to prevent any important dissociative ionization.

The main species are detected for $m/z = 1, 2, 14–16, 26–28$ and 52. That corresponds to residual nitrogen ($m/z = 28$) and methane ($m/z = 16$). Hydrocarbon radicals CH$_3$.
Figure 1. Experimental set-up.

Table 1. The main species detected in the afterglow of a mass spectrometer placed 400 mm above the discharge centre.

| m/z  | 52  | 28  | 27  | 26  | 16  | 15  | 14  | 2   | 1   |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Species | C₂N₂ | H₂CN | HCN | CN  | CH₄ | NH  | N   | H₂  | H   |
|        | C₂H₄ |      |     |     |     |     |     |     |     |


(m/z = 15) and CH₂ (m/z = 14) are produced in the reaction between ‘active’ nitrogen species and methane or H atoms (m/z = 1), H₂ (m/z = 2) and N atoms (m/z = 14), NH (m/z = 15), HCN (m/z = 27), H₂CN (m/z = 28), CN (m/z = 26) or C₂N₂ (m/z = 52) and are the result of recombination downstream of the discharge after reactions between N active species and methane. Figure 2 shows the change in the mass spectrometer intensities measured for m/z = 14–16, 26–28 and 52 versus the methane density injected downstream of the nitrogen discharge working at 100 W and a nitrogen pressure equal to 40 Pa. The most important signals are detected for m/z = 28, 15, 52, 26, 27, 16 and 14 respectively. In the case of m/z = 52 and 27 the signal intensities are constant all over the CH₄ concentration range under investigation. For the other species, the signal intensities increase with increasing methane concentration until a maximum value, then they remain constant. The maximum value is reached for a methane concentration close to 2 × 10¹⁹ m⁻³ for m/z = 15 and larger than 4 × 10¹⁹ m⁻³ for m/z = 28 and 26. In the case of m/z = 14 the signal intensity increases until a maximum value corresponding to a methane concentration equal to 1 × 10²⁰ m⁻³, then the signal intensity decreases with increasing methane concentration. The decrease of N₂ signal is expected to be low when CH₄ density increases because the discharge power remains at a constant value (100 W) during the whole experimentation time so the dissociation yield of N₂ remains unchanged. Consequently, in the case of m/z = 28, the signal intensity increase is expected to be ascribed to the increase of C₂H₄ or H₂CN species produced by the reaction of
CH₄ with ‘active’ nitrogen species. In the same way, the signal intensity increase observed for \(m/z = 14\) should not be ascribed to the increase in the density of N atoms produced in the discharge, but to the increase of the concentration of the CH₂ radicals. Moreover, according to Gartaganis [11] the main product generated in a conventional discharge fast-flow is hydrogen cyanide and the mass spectrometer failed to detect more than possible traces of substances that might have been C₂ and C₃ hydrocarbon or cyanogen. According to Pintassilgo et al [7], HCN is also one of the most abundant species detected either from spectroscopy observations of the Voyager Spacecraft or in laboratory simulation of Titan’s atmosphere. In all these cases HCN appears as the most abundant organic compound detected with either C₂H₆ (in high-energy particle experiments) or C₃H₂ (in electric discharge). It is worth noting that, according to the authors, the calculations show that the H₂CN concentration is always vanishingly small with H₂CN/HCN = 10⁻⁵. These observations agree more or less with our results. In our case, the peak corresponding to CH₃ (\(m/z = 15\)) is larger than the signal measured for \(m/z = 27\), 26 and 52 and no significant peak is observed at \(m/z = 30\). Moreover since the H₂CN concentration is very small, the large signal measured for \(m/z = 28\) is probably due to N₂ and C₂H₄. So far we have focused our work on the study of the reaction between methane and different nitrogen species in a nitrogen afterglow. In what follows, we measure the reaction rate constant of the global reaction and we study elementary processes in order to determine which ‘active’ nitrogen species are implicated in the dissociation mechanism of the methane in the discharge afterglow.
3. Results

3.1. Reactivity of CH₄ in a nitrogen afterglow

As seen above, methane reacts with ‘active’ nitrogen species in the discharge afterglow, producing various species. These species are either directly produced as CH₃ and CH₂ simple radicals in the reaction of methane with ‘active’ nitrogen species or produced by a several step reaction mechanism (radical generation and recombination) as HCN and CN. These previous species are produced after breaking CH₄ and recombining the radical produced with nitrogen species that lead to C–N bond formation. In the following, we consider CH₂ species detected for \( m/z = 14 \) and CH₃ or NH species detected for \( m/z = 15 \).

The reactive mechanisms corresponding to the global reaction producing \( m/z = i \) can be written:

\[
M + CH₄ \rightarrow k_i \rightarrow X(m/z = i) + \text{products}
\]  

(1)

where M are ‘active’ nitrogen species reacting with CH₄. \( X(m/z = i) \) is a species detected for \( m/z = i \).

Assuming that the methane density is injected in a sufficiently large amount to be considered as constant over all the reaction time, we can write the following balance equations:

\[
d(X(m/z = i)/dt = k_i(M) \cdot (CH₄) = k_iM_0(1 − \Sigma \alpha_j(t)) \cdot (CH₄)
\]

(2)

where \( (M) \) and \( (CH₄) \) are the concentration of active nitrogen species and methane respectively, \( M_0 \) is the initial value of \( (M) \), when no methane is injected and \( \alpha_i(t) \) is a parameter ranging between 0 and 1, which increases with the development of the reaction. \( \alpha_i(t) = 0 \) at the beginning \( (t = 0, M = M_0) \) and is equal to 1 at the end of the reaction \( (t = T, M = 0 \text{ m}^{-3}) \).

The value \( \Sigma \alpha_j(t) \) is the sum of all these parameters corresponding to the reaction between M and CH₄ and producing the different \( X(m/z = i) \) species concentrations corresponding to the branching ratio of the reaction.

Assuming that \( X(m/z = i) \) is mainly produced by reaction (1) and that it does not have time to recombine before being analysed, we have:

\[
X(m/z = i) = M_0\alpha_i(t) \quad \text{and} \quad d(X(m/z = i))/dt = M_0 d(\alpha_i(t))/dt.
\]

(3)

Consequently we have,

\[
d(\alpha_i(t))/dt = k_i(1 − \Sigma \alpha_j(t)) \cdot (CH₄).
\]

(4)

Using the calculation presented in the appendix, we obtain

\[
\alpha_i(t) = k_i/\Sigma(k_j)[1 − \exp(−\Sigma(k_j) \cdot (CH₄) \cdot t)]
\]

(5)

where \( t \) is the reaction time \( t = L/v = 0.01 \text{ s} \), \( L \) is the reaction pathway \( L = 195 \text{ mm} \) and \( v \) is the gas flow velocity in the reaction pathway where \( v = 20 \text{ m s}^{-1} \).

The mass spectrometer signal \( I_i \) measured for the \( i \) species is given by [12],

\[
I_i = n_i\sigma(\varepsilon_e)T(m_i, n_i).
\]

(6)

In this relation \( n_i \) is the density of \( i \) species, \( \sigma(\varepsilon_e) \) is the ionization cross section when the electron energy is \( \varepsilon_e \) and \( T(m_i, n_i) \) (unity A m) is the transmission factor of \( i \) species, depending on the mass and the density of \( i \) species.
Consequently we have,
\[
I(X(m/z = i))/I(X(m/z = i))_{\text{ref}} = \frac{\alpha_i(t)/\alpha_i(t)_{\text{ref}} = k_i/\Sigma(k_j)[1 - \exp(-\Sigma(k_j) \cdot (CH_4) \cdot t)]/\alpha_i(t)_{\text{ref}}}{[1 - \exp(-\Sigma(k_j) \cdot (CH_4) \cdot t)]/[1 - \exp(-\Sigma(k_j) \cdot (CH_4)_{\text{ref}} \cdot t)].}
\]

(7)

Figure 3. Mass spectrometer signal intensity ratio \(I(m/z)/I(m/z)_{\text{ref}}\) measured for \(m/z = 15\) and 14 versus the methane concentration injected into the nitrogen afterglow. The best adjustment between theory (curves) and experiment (points) is obtained for \(\Sigma k_j\) ranges between \(1 \times 10^{-18}\) and \(6 \times 10^{-18}\) m\(^3\) s\(^{-1}\).

In this relation the subscript ref is related to values taken as references. In our case, this value is the signal intensity measured for an injected methane concentration equal to \(1.86 \times 10^{20}\) m\(^{-3}\).

The mass spectrometer signal intensity ratio \(I(m/z)/I(m/z)_{\text{ref}}\) measured for \(m/z = 15\) and 14 versus the methane concentration injected into the nitrogen afterglow is indicated in figure 3. Considering the reactive mechanism (reaction (1), the best adjustment between theory and experiment is obtained for \(\Sigma(k_j)\) ranging between \(1 \times 10^{-18}\) and \(6 \times 10^{-18}\) m\(^3\) s\(^{-1}\).

In what follows the ‘active’ nitrogen species reacting with CH\(_4\) in such a process are determined by investigating the elementary reactive mechanisms which occur between CH\(_4\) and nitrogen species in the nitrogen afterglow. These previous species consist of vibrationally excited molecules N\(_2\)(X\(^1\Sigma_g^+\)) or metastable molecules N\(_2\)(A\(^3\Sigma_u^+\)), N\(_2\)(a\(^1\Sigma_u^+)\), N\(_2\)(a\(^1\Pi_g\)) or N atoms in the ground state \([4S]\) or in the metastable states \([2D]\) or \([2P]\) [13]. The ions are not observed in the afterglow because this is a no space charge region. The radiative species N\(_2\)(C\(^3\Pi_u\)) and N\(_2\)(B\(^3\Pi_g\)) which are also detected are expected to be not chemically efficient at this pressure range because of their too short radiative lifetimes.

According to [14] and [15], N\(_2\)(X\(^1\Sigma_g^+, v\)) species which involve 46 vibrational levels are identified as the most important species in the afterglow. Moreover they have a long lifetime. The two other species N\(_2\)(A\(^3\Sigma_u^+)\) and N(\(^4\)S) are also important. According to [15], in a dc discharge at a total pressure equal to 93 Pa and a discharge current intensity equal to 20 mA,
the gas mixture at the exit of the discharge contains 0.006\% N$_2$(A$^3\Sigma_u^+$) and 1\% N(4S). The concentration in N(2P) and N(2D) is several orders of magnitude lower than that of N(4S).

The other radiatively coupled N$_2$(a$^1\Sigma_u^-$) and N$_2$(a$^1\Pi_g$) metastable states, lying about 8.6 eV above the ground state are also largely populated in nitrogen electrical discharge [16]. At present, we cannot investigate the efficiency of all these species to dissociate CH$_4$. So in the next part of this paper, we focus our investigation on elementary processes corresponding to the reaction of N$_2$(A$^3\Sigma_u^+$) and N atoms with CH$_4$.

3.2. Reactivity of CH$_4$ with N$_2$(A$^3\Sigma_u^+$)

N$_2$(A$^3\Sigma_u^+$) is selectively produced using the well known method [17] of energy transfer from Ar($^3$P$_2$) to N$_2$

$$N_2(X^1\Sigma_g^+)+\text{Ar}^3P_2 \rightarrow N_2(C^3\Pi_u \text{ or } B^3\Pi_g) + \text{Ar}^1S_0$$

then, the radiative processes is written:

$$N_2(C^3\Pi_u \text{ or } B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + h\nu.$$  
(9)

N$_2$(C$^3\Pi_u$) and N$_2$(B$^3\Pi_g$) selectively populate the N$_2$(A$^3\Sigma_u^+$) state without creation of any atomic or vibrationally excited nitrogen molecules in the ground state by a radiative cascade producing the first and second positive system of N$_2$ [17].

In order to investigate the effect of N$_2$(A$^3\Sigma_u^+$) on the methane dissociation, we have modified the reactor and introduced another gas injector between the discharge and the methane injector.

The argon Ar($^3$P$_2$) concentration is measured by means of absorption spectroscopy at the wavelength 811.5 nm, corresponding to the transition line 4S[3/2]$^6$-4P[5/2]. The maximum metastable argon Ar($^3$P$_2$) concentration occurs using a microwave power of 20 W, a gas flow velocity of 20 m s$^{-1}$ and a total pressure of 33 Pa. Under these conditions the argon metastable Ar($^3$P$_2$) concentration is $4 \times 10^{16}$ m$^{-3}$ at 20 cm above the discharge centre. Whereas the Ar($^3$P$_0$) concentration is estimated to be about 10\% the Ar($^3$P$_2$) concentration [18].

Nitrogen is injected 20 cm above the discharge centre. The reaction is fast and total so the N$_2$(A$^3\Sigma_u^+$) concentration is equal to the Ar($^3$P$_2$) concentration (i.e. $4 \times 10^{16}$ m$^{-3}$) [17]. Then CH$_4$ is injected 10 cm downstream of the N$_2$ injector.

Investigations performed by means of a mass spectrometer within the nitrogen afterglow show that various species are produced because of the reaction between CH$_4$ and N$_2$(A$^3\Sigma_u^+$). The signal intensity measured for the different m/z species detected versus the CH$_4$ concentration injected in the afterglow is reproduced in figure 4.

The main species produced are detected for m/z = 30 and 15. That corresponds to C$_2$H$_6$ and CH$_3$ species respectively. A maximum is seen for a CH$_4$ concentration ranging between 3 and $5 \times 10^{19}$ m$^{-3}$. C$_2$N$_2$, H$_2$CN, HCN and CN species corresponding to m/z = 52, 29, 27 and 26 respectively are also detected. The signal measured for these species is much lower than for the two former species and shows a maximum for CH$_4$ concentrations lower than $1 \times 10^{19}$ m$^{-3}$. The signal intensity decreases for larger CH$_4$ concentrations. It appears that the main species produced by the reaction of CH$_4$ with N$_2$(A$^3\Sigma_u^+$) is CH$_3$ which recombines to produce C$_2$H$_6$. Initially, when a low methane concentration is injected, N$_2$(A$^3\Sigma_u^+$) reacts with CH$_4$ producing CH$_3$ which recombines to produce C$_2$H$_6$. The curve profile increases with increasing methane concentration. When a larger methane concentration is injected, all the N$_2$(A$^3\Sigma_u^+$) is quenched and the amount of CH$_3$ produced in the afterglow does not increase any more with increasing methane concentration. Here, the decrease of the CH$_3$ concentration (and consequently of

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Figure 4. Signal intensity measured for various species versus the methane concentration injected into the discharge afterglow, when CH$_4$ reacts with N$_2$($A^3\Sigma^+_u$) species.

C$_2$H$_6$) when the CH$_4$ concentration is increasing is probably due to other reactive processes which become dominant for these concentrations of injected methane.

The reaction rate constant of this reaction is equal to $4.36 \times 10^{-17}$ m$^3$ s$^{-1}$ at 300 K [19]. Thomas et al [20] have measured the vibrational relaxation of N$_2$(A$^3\Sigma^+_u$, $v = 1, 2, 3$) by CH$_4$ using the laser induced fluorescence method on N$_2$(A$^3\Sigma^+_u$, $v$). They showed that the higher the $v$ level is the faster is the rate of vibrational relaxation. They measured rate constants of 1.5, 3.1 and $5.0 \times 10^{-18}$ m$^3$ s$^{-1}$ for the quenching of N$_2$(A$^3\Sigma^+_u$, $v$), $v = 1, 2, 3$ respectively. Golde et al [21], measure a low reaction rate constant equal to $3.2 \times 10^{-21}$ m$^3$ s$^{-1}$ for the reaction of CH$_4$ with N$_2$(A$^3\Sigma^+_u$, $v = 0$). These results confirm the high reactivity of CH$_4$ with N$_2$(A$^3\Sigma^+_u$, $v > 0$). It appears that CH$_3$ species produced by the reaction of methane with this molecular vibrationally excited metastable species has probably been previously detected in the nitrogen afterglow.

In the next part of this paper we study the selective reaction of N atoms with the methane.

3.3. Reactivity of CH$_4$ with N atoms

In the method proposed by Miyazaki [22] the methane is injected into the nitrogen afterglow on N atoms. Hydrogen cyanide is mainly produced. No cyanogen, ammonium or hydrazine are detected in significant amounts

$$\text{N} + \text{CH}_4 \rightarrow \text{HCN} + 3\text{H}. \quad (10)$$

The change in the concentration of N atoms is determined by measuring the change in emission band intensity of the first N$_2$ positive system.

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Next we consider the main reactive processes for the quenching of N atoms: the Lewis–Rayleigh recombination process and the reaction between N atoms and CH$_4$ or other CH$_x$ radicals,

\[
N + N + M \rightarrow k_1 \rightarrow N_2(C^3\Pi_u, B^3\Pi_g) + M \\
N + CH_x \rightarrow k_i \rightarrow \text{products}
\]  

(11)

where M is mainly N$_2$ or CH$_4$ and x and i range between 0–4 and 2–6 respectively.

The differential form of the rate equation is written,

\[
d(N)/dt = -k_1 \cdot ((N_2) + (CH_4)) \cdot (N)^2 - \Sigma_i k_i \cdot (CH_{6-i}) \cdot (N)
\]

(12)

where \(\Sigma_i k_i(\text{CH}_{6-i})\cdot (N)\) is the sum over the i reactions of N with CH$_x$.

Writing \((N) = a - x\), with \(a\) equal to the initial N atom concentration at \(t = 0\), the former balance equation becomes

\[
d(a-x)/dt = -\{k_1(a-x)^2 \cdot [(N_2) + (CH_4)] - \Sigma_i k_i \cdot ((a-x) \cdot (CH_{6-i}))\}.
\]

(13)

Assuming that the methane concentration is constant through the previous reaction. Under this condition integration of (13) gives,

\[
\ln\{1 - k_1 \cdot ((N_2) + (CH_4)) \cdot x/[k_1 \cdot ((N_2) + (CH_4)) \cdot a + \Sigma_i k_i \cdot (CH_{6-i})]\} + \ln\{a/(a-x)\} = \Sigma_i k_i \cdot (CH_{6-i}) \cdot t
\]

(14)

where \(a\) and \((a-x)\) are the nitrogen atom concentration at the beginning of the reaction and at the time \(t\) respectively. Assuming that the nitrogen atom concentration in the afterglow, according to the recombination kinetics is proportional to the rate of disappearance of the nitrogen atoms, i.e. to the product \(N^2\), we have \((a-x)/a = (I/I_0)^{1/2}\), where, \(I_0\) and \(I\) are the emission band intensity of a transition of the first positive system measured with and without CH$_4$ injected respectively.

Using the parameter \(\beta_i\), defined as \(\beta_i = (\text{CH}_{6-i})/(\text{CH}_4)\), equation (14) becomes

\[
f(I/I_0) = \ln\{1 - [k_1 \cdot ((N_2) + (CH_4)) \cdot a(1 - (I/I_0)^{1/2})]/[k_1 \cdot ((N_2) + (CH_4)) \cdot a + \Sigma_i k_i \beta_i \cdot (CH_4)]\} + \ln\{(I_0/I)^{1/2}\} = \Sigma_i k_i \beta_i \cdot (CH_4) \cdot t.
\]

(15)

Initially, we measured the density of N atoms in the nitrogen afterglow using the well known NO titration method [23, 24]. No gas is mixed with the N$_2$ gas downstream from the plasma. Because the reaction NO + N → N$_2$ + O is faster than all other relevant reactions, NO gas scavenges atomic nitrogen. When the NO concentration exceeds the N concentration, the excess NO reacts on the atomic oxygen of the previous reaction producing NO$_2$. The concentration in N atoms is determined measuring the NO flow rate at which the NO$_2$ mass spectrometer peak becomes observable. Using this method, we have determined a density of N atoms equal to \(4.8 \times 10^{13}\) cm$^{-3}$ at \(P = 40\) Pa and for an incident power equal to 100 W. Measurements have been performed 40 cm downstream from the discharge centre, i.e. 19 cm above the methane injector.

The main processes of N atom quenching when no CH$_4$ is fed into the reactor is the Lewis–Raleigh recombination process \((N + N + M \rightarrow N_2 + M)\) in the bulk and N atom wall recombination on the tube wall. In the case of the Lewis–Raleigh recombination process, using the reaction rate constant value given in the literature \(k = 1.45 \times 10^{-14}\) m$^{-6}$ s$^{-1}$ [15, 22]. A brief calculation shows that the N atom density at the methane injector is about the same as the N atom density measured at the mass spectrometer sample hole \(N = 4.8 \times 10^{13}\) cm$^{-3}$ in these experimental conditions and assuming that the gas flow velocity is equal to 20 m s$^{-1}$. According
Figure 5. $f(I/I_0)$ versus the methane concentration injected within the nitrogen afterglow. The microwave power is 100 W and the nitrogen pressure is equal to 40 Pa. The best adjustment is obtained for $\Sigma_i k_i \beta_i$ ranges between $2 \times 10^{-18}$ and $3 \times 10^{-18}$ m$^3$ s$^{-1}$.

Figure 5 shows $f(I/I_0)$ versus the concentration of CH$_4$ injected into the nitrogen afterglow. The nitrogen pressure is 40 Pa and the microwave pressure is 100 W. Results are compared to calculations obtained using equation (15) with $k_1$ equal to $1.45 \times 10^{-44}$ m$^6$ s$^{-1}$ [22]. Assuming in a first approximation that $\beta_i$ is constant for all CH$_x$ species in the range of methane concentration under investigation, the best agreement between the theory and the experimentation is obtained for $\Sigma_i k_i \beta_i$ ranges between 2 and $3 \times 10^{-18}$ m$^3$ s$^{-1}$. This result is greatly different from the value given in the literature, $1.06 \times 10^{-22}$ m$^3$ s$^{-1}$ [22] measured in the case of the reaction between an N atom and CH$_4$ molecule. According to Stief et al [26] or Marston et al [27], the N atom is mainly destroyed in a nitrogen afterglow by reaction with hydrocarbon free radicals. These should be produced by the reaction between CH$_4$ and metastable N$_2$(A$^3\Sigma^+_u$) and/or H atoms. The authors have studied the reaction of N with CH$_3$ and show that the reaction produces mainly H$_2$CN which accounts for 90% of the reaction, with a minor channel (10%) producing HCN. They give
Table 2. Reaction rate constant values given in the literature for different reactions between N and radicals CH, CH₂ and CH₃.

| Radical | Reaction rate constant (m³ s⁻¹) | Reference |
|---------|---------------------------------|-----------|
| CH      | 2.1 × 10⁻¹⁷                     | [28]      |
| CH₂     | 8.3 × 10⁻¹⁷                     | [29]      |
| CH₃     | 8.5 × 10⁻¹⁷                     | [27]      |

for the reaction rate constant a value of 8.5 × 10⁻¹⁷ m³ s⁻¹. This value is in better agreement with our result. Table 2 gives other reaction rate constant values measured for the reaction of N atom with various free radicals (CH, CH₂, CH₃). These results are in better agreement with our values than the value given by Miyazaki [22]. The large value that we measured in the nitrogen afterglow for Σ₁kᵢβᵢ shows that probably N atoms do not react only with CH₄ but also with CHₓ species. In order to explain this behaviour, we propose the following mechanism. CH₄ is injected in a region downstream of the discharge containing N₂(A³Σ⁺ᵤ) in such a concentration that it reacts efficiently on the methane producing free radicals CH, CH₂ or CH₃. Then these radicals react with N atoms producing H₂CN or HCN. These results suppose that Miyazaki [22] worked under experimental conditions producing no N₂(A³Σ⁺ᵤ) at the injector position. However, no information concerning the position of the methane injector is given in [22] and it is impossible to check the accuracy of this assumption. These authors worked at a higher nitrogen pressure (about 400 Pa) and a lower flow velocity of around 0.5 m s⁻¹, and these conditions are more favourable for the efficient ‘pooling’ recombination process of N₂(A³Σ⁺ᵤ) [15] downstream of the flowing discharge in N₂.

4. Conclusion

The reactivity of CH₄ in a nitrogen afterglow is efficient. Investigations have been performed using selective reactions in order to explain the reactive scheme involved in such a process. We have measured a reaction rate constant value for the global reaction between CH₄ and ‘active’ nitrogen species ranging between 1 × 10⁻¹⁸ and 6 × 10⁻¹⁸ m³ s⁻¹. This value is of the same order as the value given in the literature and corresponding to the reaction of vibrationally excited N₂(A³Σ⁺ᵤ) (v = 1, 2, 3) and CH₄. Moreover we have shown that in this case this reactive process produces a large amount of CH₃. The decay of the N atom concentration in the afterglow when CH₄ is injected corresponds to a reaction rate constant value ranging between 2 and 3 × 10⁻¹⁸ m³ s⁻¹, which is larger than the rate constant of the reaction between N atoms and CH₄ [22] and of the same order as the reaction between N atoms and simple radicals CHₓ<₄ (see table 2). This is correlated to the CH₄–N₂(A³Σ⁺ᵤ, v > 0) reaction in the nitrogen afterglow producing simple radicals CHₓ<₄ (mainly CH₃), which react with N atoms producing H₂CN or HCN.

We propose the following mechanism. To begin with, CH₄ injected in the nitrogen afterglow reacts with the metastable N₂(A³Σ⁺ᵤ) producing radicals CHₓ<₄. In this initial reaction, vibrationally excited metastable N₂(A³Σ⁺ᵤ, v) states which are in large concentration at the discharge exit seems to be efficient in the dissociation process because of the high reaction rate constant proposed in the literature (1.5–5 × 10⁻¹⁸ m³ s⁻¹). In a second step, the simple radical
produced reacts with N atoms producing mainly H₂CN and HCN. The reaction is also very efficient because the reaction rate ranges between 2 and 3 × 10⁻¹⁸ m³ s⁻¹.

According to the literature [30], other molecular metastable species N₂(a¹Πg) or N₂(a'¹Σ⁻u) are produced in a nitrogen discharge. N₂(a¹Πg) is highly populated and more specifically in the vibrational state \( v = 1 \) because of the atomic recombination process and this electronic state is efficiently quenched in the second electronic state N₂(a'¹Σ⁻u) [31]. These two states can also be implicated in the dissociation of CH₄ in the nitrogen afterglow. According to the literature [31, 32], the reaction of these two metastables with CH₄ is efficient. The reaction rate constant values are 5.2 × 10⁻¹⁶ and 3 × 10⁻¹⁶ m³ s⁻¹ in the case of reaction with N₂(a¹Πg) and N₂(a'¹Σ⁻u) respectively. These two species can also play a significant role in the CH₄ dissociation in a nitrogen discharge.

Appendix

If we consider a global CH₄ dissociation for the reaction (1), the \( \alpha(t) \) global parameter is given by \( \alpha(t) = \Sigma \alpha_j(t) \) and we can write using (4),

\[
d(\alpha(t))/dt = d(\Sigma \alpha_i(t))/dt = \Sigma d(\alpha_i(t))/dt = \Sigma (k_i \cdot (1 - \Sigma \alpha_j(t)) \cdot (CH_4)) = \Sigma (k_i \cdot (1 - \alpha(t)) \cdot (CH_4)).
\] (A.1)

After integration over the reaction time between 0 and \( t \), we have the following analytical relation

\[
\alpha(t) = 1 - \exp(-\Sigma(k_i) \cdot (CH_4) \cdot t).
\] (A.2)

Using (4), we can see that whatever \( i \) and \( j \) species are

\[
d(\alpha_i(t))/d(\alpha_j(t)) = k_i/k_j.
\] (A.3)

If we write \( \alpha(t) \) as follows

\[
\alpha(t) = \alpha_1(t) + \alpha_2(t)
\] (A.4)

where \( \alpha_1(t) = \alpha_i(t) \) and \( \alpha_2(t) = \Sigma \alpha_m(t) \) where \( m \) is different from \( i \), so we have the derivation of \( \alpha(t) \)

\[
d(\alpha(t))/dt = -\Sigma(k_j) \cdot (CH_4) \cdot \exp(-\Sigma(k_j) \cdot (CH_4) \cdot t) = d(\alpha_1(t) + \alpha_2(t))/dt
\] (A.5)

where \( k_2 = \Sigma(k_m) \) with \( m \) different from \( i \).

Consequently, we have

\[
\alpha_i(t) = k_i/\Sigma(k_j) \cdot [1 - \exp(-\Sigma(k_j) \cdot (CH_4) \cdot t)]
\] (A.6)

where \( t \) is the reaction time \( t = L/v = 0.01 \) s, \( L \) is the reaction pathway \( L = 195 \) mm and \( v \) is the gas flow velocity in the reaction pathway with \( v = 20 \) m s⁻¹.

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