REMPI DETECTION OF CH_3 IN LOW-PRESSURE FLAMES

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This study presents results on the detection of CH_3 in low-pressure methane–oxygen flames using resonance-enhanced multiphoton ionization (REMPI) techniques. Experiments in a discharge-flow reactor were performed for optimization purposes. Excitation wavelengths near 286 and 333 nm were examined; the former is not recommended for flame applications, although it may be preferable under flow reactor conditions.

1. Introduction

The methyl radical (CH_3) is an important intermediate in hydrocarbon combustion. For example, in methane flames CH_3 recombination may be a key step in the formation of two-carbon species. For detailed chemical-kinetic flame modelling, it is desirable to develop techniques which allow the determination of CH_3 concentration profiles.

As methyl radicals do not exhibit fluorescence, resonance-enhanced multiphoton ionization (REMPI) has been used by several groups to detect CH_3 under different conditions, e.g. in the photodissociation of CH_3I [1,2] or CH_3NO_2 [3]. Thorough investigations of the REMPI spectroscopy of the CH_3 radical have been undertaken by Hudgens and co-workers [4–6], who used a discharge flow reactor or thermal decomposition of various compounds in an oven as the CH_3 source. All these studies have used a mass spectrometer in connection with the ionization detection to assign unambiguously the spectral features. Recently, Chou [7] detected CH_3 in high-temperature methane pyrolysis. The first and, to our knowledge, only REMPI flame investigation has been performed by Smyth and Taylor [8] in a CH_4/air diffusion flame. The authors were able to detect CH_3 low down in the flame, but at larger distances from the burner outlet the REMPI signal was completely obscured by non-resonant background ionization. In a recent study from the same laboratory [9], CH_3 profiles were obtained by a scavenger microprobe technique in agreement with the profiles measured earlier by REMPI. Although this probe technique was capable of detecting CH_3 throughout the flame, it did not offer the same spatial resolution as the optical method.

In our opinion further investigations are necessary to examine the potential of CH_3 concentration measurements by REMPI techniques in flames. In the present study, our aim was to detect CH_3 in flat, premixed low-pressure flames, where we had already measured local temperature and OH concentration profiles [10] and where measurements of H and O atom concentrations are presently being performed in our laboratory [11]. Eventually, a method which allows the measurement of CH_3 concentrations would considerably extend the experimental data on which detailed chemical-kinetic flame modelling could be based.

Two wavelength regions have been used for CH_3 REMPI detection in a (2+1) process, both exciting Rydberg states as the intermediate resonance level [6]. The transition involving the $3p\,^2A_2''$ Rydberg level requires radiation near 333.4 nm, and the $4p\,^2A_2''$ Rydberg level can be excited by two photons of 286.3 nm radiation. In both the pyrolysis and the flame study [7,8], 333.4 nm radiation has been used for CH_3 detection. The shorter wavelength near 286 nm seems attractive, as it can be easily produced with

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high laser intensity. On the other hand it is known [12] that focused short wavelength radiation may perturb the flame by inducing photodissociation. The strategy followed in the present study was to investigate the potential of both excitation schemes for the detection of CH_3 in low-pressure flames, preceded by identification and optimization experiments in a discharge flow reactor, where a lower influence of interference by other species can be expected due to the less complex chemical environment.

2. Experiment

Both the flame and flow reactor apparatus have been described previously [10,13]. Here, only the details relevant for the present experiments will be described.

The radiation was generated using a Nd:YAG-laser-pumped dye laser system equipped with a frequency doubling unit and a Raman shifter cell (Quanta Ray). For 286 nm excitation, typically 15–20 mJ were obtained by frequency doubling the radiation of a mixture of rhodamine 6G and rhodamine B. Radiation at 333 nm was produced in two different ways. By frequency doubling the radiation of red dyes such as DCM or oxazine 1, we obtained 1.2 mJ at 333 nm. With our laser system it was more efficient to use the frequency-doubled radiation of sulforhodamine B, which was then Raman shifted in H_2. The first Stokes beam near 333 nm yielded 2–2.5 mJ pulse energy.

Methyl radicals were generated in the flow reactor by one of the following reactions:

$$CH_4+F\rightarrow CH_3+HF\,, \qquad (1)$$

$$CH_3I+H\rightarrow CH_3+HI\,. \qquad (2)$$

The F or H atoms were produced in a microwave discharge in helium doped with small amounts of either F_2 or H_2. Reaction (2) is nearly as fast [14] as the more commonly used reaction (1) and was preferred because the spectra of impurities in the vicinity of the CH_3 band were in this case much less significant (see below).

Ionization signals were detected by a probe adapted from Cool [15]. Two slightly different versions of this probe were used, one with platinum and the other with molybdenum electrodes. Both had a load resistor of 150 kΩ. Typical experimental conditions required a probe voltage of 300–500 V. Excitation at 286 nm resulted in ionization signals of the order of 0.5–1 V. At 333 nm, signals of 1–5 mV were obtained, which were then amplified by factors of 100–200. Signal recording was performed with either a transient digitizer (Tektronix R7912) or a boxcar integrator (Stanford Research Systems), both with 1 MΩ input impedance. The probes were not exposed directly to the flame in order to avoid rapid degradation.

3. Results and discussion

The experimental results obtained in the flow reactor and the flame will be described successively for each of the two wavelength regions.

3.1. CH_3 detection at 286 nm

In the discharge flow reactor, we first generated CH_3 by the reaction of methane with fluorine atoms. At 1 mbar, approximately 10^{14} CH_3/cm^3 were produced. The CH_3 spectrum exhibited the expected single sharp peak [6] near 286.3 nm. The wavelength scale was calibrated by recording two-photon excitation spectra of hydrogen atoms at 205 nm using the same laser dyes. Close to the CH_3 spectrum, several spectral features were detected at slightly longer wavelengths, which apparently were not associated with CH_3. These signals responded in the same way to methane, fluorine, or fluorine atom concentration changes as well as to changes in the microwave discharge power of the CH_3 ionization signal, but disappeared when reaction (2), with methyl iodide and hydrogen atoms, was used. We did not investigate the nature of this impurity spectrum, but we subsequently preferred the use of reaction (2) for further experiments. From the data obtained in the flow reactor, the detection limit for CH_3 is estimated to be below 10^{12} cm^{-3}.

In a slightly rich methane–oxygen flame at 40 mbar, a considerable number of almost evenly spaced lines were observed between 284 and 288 nm, which were strongest in intensity close to the burner surface. These lines did not disappear throughout the

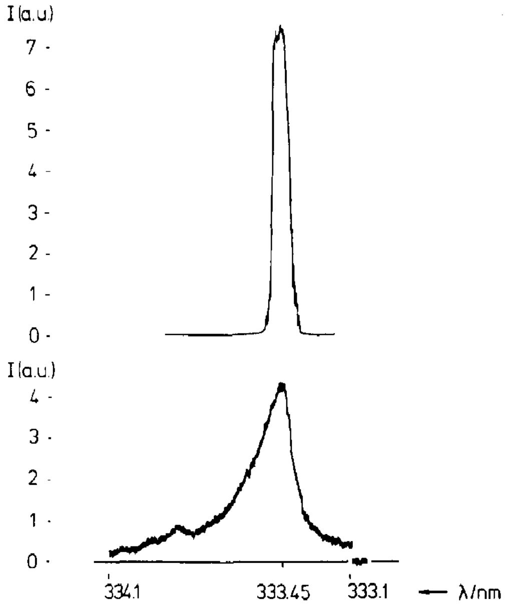

Fig. 1. CH_3 REMPI spectrum near 333 nm. Upper trace: discharge flow reactor at $p=3.4$ mbar, production of CH_3 by the reaction of CH_3I with H atoms; lower trace: 40 mbar CH_4/O_2 flame, $\Phi=1.2$, height above the burner $h=0.6$ nm.

flame, and were still present in the burnt gases. This spectral structure was found to be identical in a slightly rich ethane–oxygen flame, and it was also observed in a lean hydrogen–oxygen flame. Clearly, the spectrum could not be associated with CH_3. Due to this persistent background, the origin of which was not investigated, we did note use this wavelength region for further flame studies.

3.2. CH_3 detection at 333 nm

In the flow reactor, we obtained one single spectral feature near 333 nm, which was identical for both reactions (1) and (2). No additional lines were found in the vicinity of this peak. The measured peak wavelength agreed very well with the energy difference reported [6] for the two-photon resonant transition. The Q branch of the 3p $^2A_2''$ $0_0^0-\tilde{X}\,^2A_2''$ transition of CH_3 is shown for a pressure of 3.4 mbar in the upper part of fig. 1; in this case, methyl iodide was used as the CH_3 precursor.

For the production scheme with methane and fluorine atoms, the CH_3 signal increased linearly with methane concentration, until the initial fluorine atom concentration was consumed. For higher methane concentrations, a maximum, followed by a slight decrease of the signal, was observed. A similar behaviour was found for the signal variation with fluorine concentration.

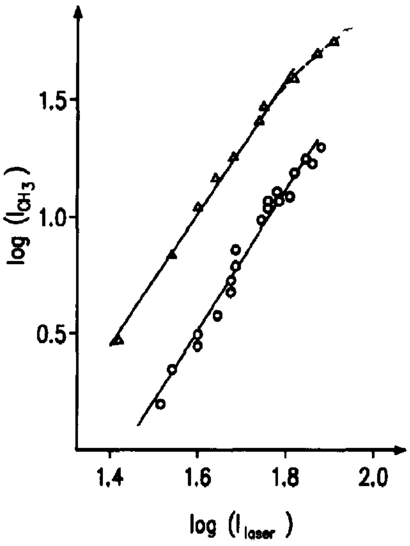

Fig. 2. Dependence of the CH_3 REMPI signal intensity on the laser intensity (log–log scale). △, discharge flow reactor, $p=3.4$ mbar; slope: 2.97 ± 0.07; ○, CH_4/O_2 flame, $\Phi=1.2$, $p=40$ mbar; slope: 3.02 ± 0.11

The ionization signal increased non-linearly with pressure and exhibited a maximum near 20 mbar. As displayed in the upper part of fig. 2, the CH_3 ionization signal intensity increased by three orders of magnitude with the laser intensity, as expected for a three-photon process, as long as the ionization step was not saturated. The detection limit in the flow reactor is estimated to be approximately 10^{12} cm^{-3}.

A REMPI spectrum of CH_3 obtained in a 40 mbar methane–oxygen flame of equivalence ratio $\Phi=1.2$ is shown in the lower trace of fig. 1. It is considerably broadened at flame temperatures compared to the spectrum measured under flow reactor conditions. No additional spectral features were observed in the flame close to the wavelength region shown in fig. 1. The measured spectral width is in good agreement with both the pyrolysis data of Chou [7] and the diffusion flame investigation of Smyth and Taylor [8]. The spectrum was only observed close (< 2 mm) to the burner surface. It was not detected in acetylene–oxygen flames at the same stoichiometry and pres-

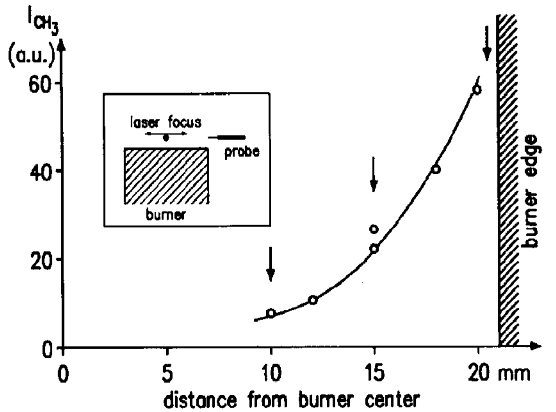

Fig. 3. CH_3 ionization signal versus distance between laser focus and probe; the probe was kept at a fixed distance to the burner (see insert). CH_3 ionization signal profiles versus height above the burner surface were taken at the positions marked with an arrow (see fig. 4).

Fig. 4. CH_3 ionization signal versus height above the burner surface in a CH_4/O_2 flame at $\Phi = 1.2$ and $p = 40$ mbar; the different symbols correspond to the profiles recorded at different distances between the laser focus and the probe (see the arrows in fig. 3).

sure, where flame model calculations indicate that the CH_3 concentrations should be more than an order of magnitude lower than in the methane–oxygen flame, and it was not found in hydrogen–oxygen flames. The dependence of the ionization signal intensity on the laser intensity scaled by a factor of 10^3, as shown in the lower part of fig. 2.

For the measurement of spatially resolved profiles of the CH_3 ionization signal as a function of height above the burner surface, we kept the ionization probe tip just outside the flame at a fixed distance from the burner centre. This arrangement avoids a priori perturbation of the flame by the probe. By translating the whole burner–probe system relative to the laser beam in the radial direction, we could vary the radial position of the laser focus, and thus the location of the CH_3 resonant multiphoton ionization, with respect to the burner centre and the probe. This configuration is sketched in the insert in fig. 3. The dependence of the ionization signal as a function of height above the burner surface could be measured by keeping the burner housing, the probe, and the laser focus fixed to each other, and translating the burner vertically.

Fig. 3 shows the decrease in the CH_3 ionization signal as a function of the radial distance between the laser focus and the probe. Vertical CH_3 ionization signal profiles were recorded at the three different radial positions marked with arrows. The normalized vertical CH_3 REMPI signal profiles obtained in this way for the three radial laser focus positions are shown in fig. 4. The three curves agree within experimental accuracy; the statistical uncertainty of the data points was about ±15%. Non-resonant background ionization scans were taken at the same locations and have been subtracted from the values shown in fig. 4. Background ionization was not a severe problem. A typical ratio of REMPI signal peak to background ionization of more than 10 can be extracted from the flame REMPI spectrum in fig. 1. The fact that the profiles recorded at three different radial positions do not differ within experimental accuracy indicates that close to the burner surface the flame is sufficiently flat; this observation was confirmed by monitoring radial OH concentration profiles.

The shape of the profiles in fig. 4 were the same, within experimental error, when the platinum wired probe was used instead of the molybdenum one. Similar dependences of the CH_3 REMPI signal on the height above the burner were obtained for methane–oxygen flames at different equivalence ratios; in each case, the signal intensity was found to decrease rapidly in the direction of the burnt gases, before the H or OH concentration maxima were attained.

Further experiments will investigate the influence of probe parameters such as size, material, and voltage and of flame parameters such as stoichiometry, temperature, and pressure on the CH_3 REMPI signal in more detail. A suitable calibration of the CH_3 profiles in fig. 4, which takes these parameters into account, will transform the measured ionization signals to relative CH_3 concentrations. The influence of the above parameters on the ionization signal can be investigated by a comparison of two-photon excited fluorescence signals with (2+1)-REMPI signals from suitably selected molecules or atoms. For example, the fluorescence signals of H atoms can be converted into concentrations, as we have shown [11]. Such experiments, performed under the same flame conditions as the CH_3 experiments, could be extremely useful in a systematic study of the ionization probe response to changing chemical and physical conditions. Similar experiments might involve stable species as CO or NO, which are present in some of the flames or could be seeded into them in necessary amounts. Relative CH_3 concentration profiles obtained in this way would be of considerable interest for chemical-kinetic flame modelling.

Measurements of absolute CH_3 concentrations in flames could be based on similar calibration schemes as for H and O atoms [11,13], where the fluorescence signals from known atom concentrations in the flow reactor are related to those in the flame, considering the influence of different chemical environments, pressure and temperature in both systems. It has been shown [16] that CH_3 can be quantitatively determined in the flow reactor by titration with NO_2. If the necessary ionization probe parameters can be extracted from experiments as described above, and if conditions can be retained where the probe does not perturb the flame, the determination of absolute CH_3 concentrations under flame conditions seems achievable.

4. Summary

The detection of CH_3 radicals by REMPI has been investigated in two different wavelength regions under flow reactor and flame conditions. Whereas excitation at 286 nm is considered promising for flow reactor experiments, excitation at 333 nm was found to be preferable for flame studies. CH_3 ionization profiles were recorded in low-pressure methane/oxygen flames. For these conditions, the ionization probe did not perturb the flame to a niticeable extent, and non-resonant ionization background was at least a factor of ten lower than REMPI signals. Further experiments will attempt a calibration of the REMPI signals in order to obtain CH_3 relative and eventually absolute concentrations, which will then be compared with flame model calculations.

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