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Determination of N-atom concentrations in low-pressure premixed $H_2/O_2/N_2$ flames doped with NH_3, HCN and $(CN)_2$

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Spatially resolved N-atom concentration and temperature profiles were measured in several stoichiometric, flat, premixed, low-pressure $H_2/O_2/N_2$ flames doped with small amounts of N-containing fuels. Temperature was obtained from OH ($A\,^2\Sigma^+$–$X\,^2\Pi$, 1–0) excitation spectra. N atoms were detected by two-photon laser-induced fluorescence, exciting the $3p\,^4D^\circ_{7/2}$ state near 211 nm and monitoring the ($3p\,^4D^\circ$–$3s\,^4P$) transition near 870 nm. N-atom concentrations were determined with the aid of a calibration technique using known atom concentrations in a discharge flow reactor and previously determined quenching coefficients. In the flames, peak N-atom mole fractions ranged from about 3 to 90 ppm.

1. Introduction

The light atoms H, O, N and C are important intermediates in combustion. They are of influence in processes such as ignition, flame propagation, and formation of soot or gaseous pollutants. The N atom, in particular, plays a role in the conversion of fuel-bound nitrogen to NO_x or N_2.

N atoms have been detected by ESR in flow systems [1] and, more recently, in flames [2]. In the latter study, the N-atom mole fraction in a Bunsen-type methane/air flame doped with NH_3 was found to be very small (about 5×10^{-8}), 3–4 orders of magnitude lower than that of H atoms in this flame. With the ESR method, the spatial distribution of the atom concentration cannot be determined. Spatially resolved measurement of light-atom concentrations in flames is possible with two-photon laser-induced fluorescence. Numerous publications have reported the detection of H and O atoms by these techniques [3,4]. N atoms, being far less abundant in flames, have been studied primarily in flow reactors [5,6]. Very recently, N atoms have been observed in a rich, premixed, atmospheric-pressure NH_3/O_2 flame by two-photon laser-induced stimulated emission [7]. While this investigation demonstrates the high sensitivity of this interesting optical technique, it is not clear how the measured N-atom signals can be converted to absolute N-atom concentrations.

Using the same excitation/detection scheme as Bischel et al. [5], we recently measured N-atom fluorescence intensity profiles in low-pressure, premixed, flat H_2/O_2N_2 flames doped with NH_3, HCN, or $(CN)_2$ [8]. The flame conditions were designed to allow a comparison of the measured N-atom profiles with current chemical-kinetic models. In the previous paper [8], lower limits of the N-atom concentrations were obtained from the fluorescence signals on the basis of a calibration technique developed previously in our group for the quantitative detection of H and O atoms in flames [4]. Without accurate values for the two-photon excitation rate and for the three-photon ionization rate as well as information on the position-dependent quenching in the flames investigated, absolute N-atom number densities could not be determined [8].

Quantitative N-atom concentrations are given in the present report. For this, calibration factors were determined for the different flame conditions of ref. [8], using measured temperatures, calculated stable-

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species profiles and estimated excitation and ionization rates. The sensitivity of the calibration to uncertainties in these quantities is discussed.

2. Experiment

The experimental arrangement has been given in detail in ref. [8]. N atoms were excited in the ($2p^3\,{}^4S^o$–$3p\,{}^4D^o$) transition near 211 nm and detected at right angles to the laser beam using the fluorescence to the $3s\,{}^4P$ state near 870 nm. The laser was operated at moderate power densities (typically 1×10^8 W cm^{-2}) to minimize photodissociation of N-atom precursors in the flames. The spectrally unresolved fluorescence was monitored through a suitable interference filter with a Hamamatsu R 636 photomultiplier. After amplification by a factor of 50, the fluorescence signal was recorded either by a fast transient digitizer (Tektronix R7912) or by a gated integrator (Stanford Research Systems SR-250). Whereas time-resolved fluorescence decays were measured in quenching and calibration experiments, time-integrated fluorescence signals were used for the measurement of N-atom profiles.

3. Results and discussion

In this study, four stoichiometric, flat, premixed $H_2/O_2/N_2$ flames were investigated, one burning at 96 mbar which was doped with 7.6% NH_3, and three at 33 mbar, doped with 0.6% NH_3, HCN, or $(CN)_2$, respectively. Similar undoped flames at 96 mbar have been studied previously [4]. The lower pressure was chosen because the flames were further away from the burner surface; also, the HCN-doped flame at 33 mbar is quite similar to that described by Miller et al. [9]. Spatially resolved temperature profiles in these flames were measured using OH ($A\,{}^2\Sigma^+$–$X\,{}^2\Pi$, 1–0) excitation spectra as described in previous publications [10]. Accurate temperature measurement not only is necessary to convert fluorescence intensity to N-atom number density and mole fraction but also is needed as an input parameter for flame model calculations.

Absolute N-atom concentrations were determined applying a calibration procedure based upon known N-atom concentrations in a discharge flow reactor in a similar way as used before H- and O-atom experiments [4]. For the calibration, the fluorescence intensities in the flame and the flow reactor, I^F and I^R, were measured under identical excitation and detection conditions. The N-atom concentration in the flow reactor, N^R, was determined by gas-phase titration with NO. The local N-atom concentration in the flame is then given by

$$N^F=(I^F/I^R)N^RC_Q\,, \qquad (1)$$

where C_Q is a calibration factor which considers the different fluorescence quantum yields in both systems. Collisional quenching is the main parameter of influence on C_Q. As chemical composition, temperature, and density change with position in the flame, the effective quenching rate k_{eff} and, thus, C_Q are position-dependent. Fig. 1 illustrates this for the flame at 96 mbar and the spatial range of interest for the N-atom profile. The upper panel shows the measured temperature profile and the mole fractions of the main constituents, N_2, H_2, O_2, H_2O and NH_3, which were calculated with a flame code [#1] using the measured temperature profile as an input. The reaction mechanism used in the calculation is that given in the recent review by Miller and Bowman [11].

The lower panel shows the contributions of the individual colliders to the effective quenching rate $k_{eff}=\sum_i k_{Q,i}N_i$. The products $k_{Q,i}N_i$ of quenching-rate coefficient $k_{Q,i}$ times number density N_i of species i were obtained using the calculated mole fractions, the experimental temperature profile, and the individual quenching-rate coefficients measured in the flow reactor at room temperature [8]. It can be seen from fig. 1 that H_2O (with the largest quenching-rate coefficient) and N_2 (with the largest number density) deliver the highest individual contributions. While k_{eff} changes by about a factor of 3.5 over the first 6 mm above the burner surface, the calibration factor C_Q varies by about 40%.

A potential temperature dependence of the quenching coefficients has been neglected in the calculation of C_Q. If this is appropriate, and if the calculations give the true mole fractions of all important colliders, the sum $\sum_i k_{Q,i}N_i$ should be equal to

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[#1] The 1990 version of the code by Professor J. Warnatz, University of Stuttgart, Germany, was used in the calculations.

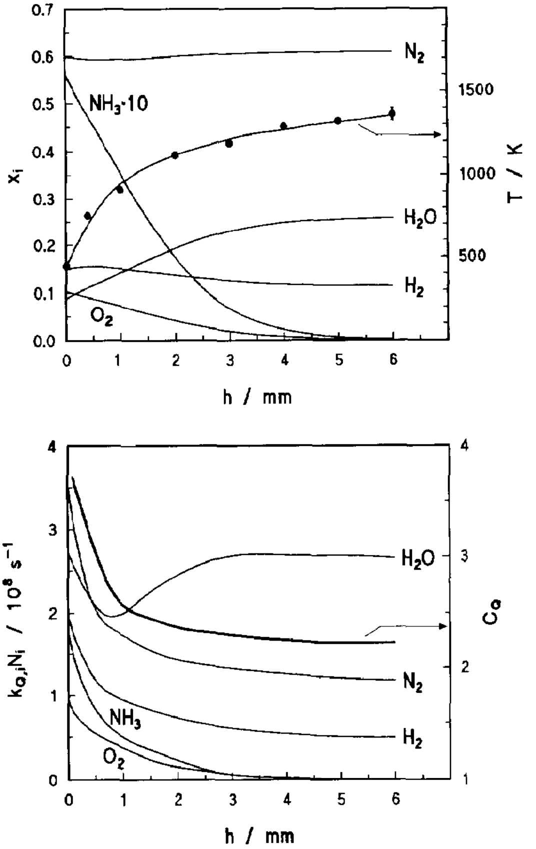

Fig. 1. Upper panel: Measured temperature profile (●) and calculated (see footnote 1 and ref. [11]) mole fractions of stable constituents for the stoichiometric 96 mbar $H_2/O_2/N_2$ flame doped with NH_3. The error bar in the temperature measurement represents 1σ. Lower panel: Contributions $k_{Q,i}N_i$ of individual colliders i to the effective quenching rate $k_{eff}=\sum_i k_{Q,i}N_i$ and calibration factor C_Q versus height above the burner surface.

the fluorescence decay rate τ^{-1}. This was examined for several locations in the flame at 96 mbar doped with NH_3 and at the position of the peak N-atom signal in the 33 mbar flame doped with $(CN)_2$. It should be noted, however, that the limited time resolution of our apparatus precludes a direct measurement of the fluorescence lifetime. Measured fluorescence decays were approximated by calculated ones using different effective quenching rates and the measured temporal-response function of the detection system. In the $(CN)_2$-doped 33 mbar flame at $h=5$ mm, $\sum_i k_{Q,i}N_i$ and τ^{-1} differ by about 10%. In the 96 mbar flame, the uncertainty in estimating the fluorescence decay rates τ^{-1} is about a factor of 1.7 and $\sum_i k_{Q,i}N_i$ and τ^{-1} agree within this range. The corresponding error in C_Q is about 5% in the 33 mbar flame and about 25% in the 96 mbar flame.

The calibration factor C_Q also is sensitive to the laser power density and to the cross sections for two-photon excitation and for photoionization by a third photon, which are not well known. This problem is addressed in detail in ref. [8]. Fortunately, C_Q is only weakly dependent on these quantities in the present experiments. Fig. 2 shows C_Q as a function of the effective quenching rate k_{eff} for typical experimental conditions. The straight line was calculated with the highest experimental laser power density of 2×10^8 W cm^{-2}, a two-photon excitation cross section of 9×10^{-28} cm^4 W^{-1} [5] and an estimated photoionization cross section of 2×10^{-19} cm^2 [8]. Changes in the cross sections by factors of 3 change C_Q by less than 20%; also, a decrease in laser power density during an experiment by as much as a factor of 3 changes C_Q only by about 15%. With C_Q being the only unknown in eq. (1), we conclude that the overall error in the determination of absolute N-atom concentrations is on the order of a factor of two.

Fig. 3 shows the N-atom profile in the NH_3-doped flame at 96 mbar. The peak number density of 5.0×10^{13} cm^{-3} corresponds to a mole fraction of about 8.7×10^{-5}. As can be seen by comparison with

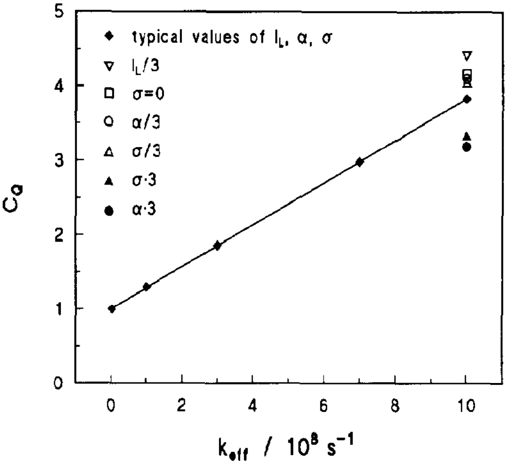

Fig. 2. Calibration factor C_Q versus effective quenching rate k_{eff} for typical values of laser power density I_L, two-photon excitation cross section α, and photoionization cross section σ: $I_L=2\times10^8$ W cm^{-2}, $\alpha=9\times10^{-28}$ cm^4 W^{-1}, $\sigma=2\times10^{-19}$ cm^{-2}.

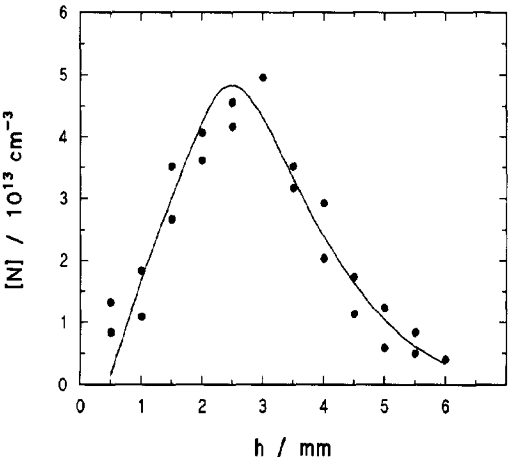

Fig. 3. N-atom concentration in the NH_3-doped flame at 96 mbar versus height above the burner surface.

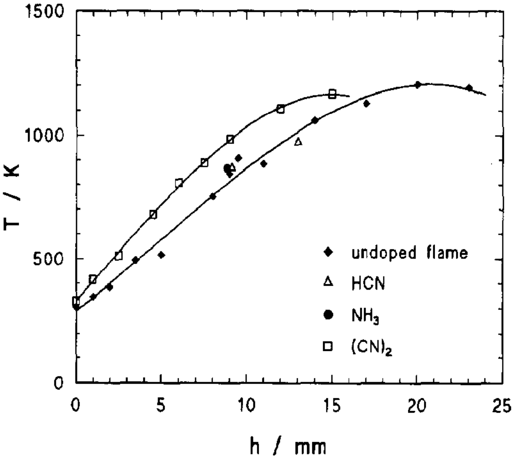

Fig. 4. Temperature versus height above the burner surface in the 33 mbar flames.

fig. 1, the N atoms are present in the zone of the steep temperature rise, with most of the additive being already consumed. The measured temperatures in the 33 mbar flames are shown in fig. 4. While the small amounts of NH_3 and HCN do not change the temperatures in comparison to the undoped flame, the $(CN)_2$-doped flame burns at slightly higher temperatures. Fig. 5 gives the N-atom concentration profiles in the 33 mbar flames. To facilitate the comparison, they are scaled to a common maximum of 1.0. While fluorescence intensity profiles have been shown in a similar plot in ref. [8], position-dependent calibration factors have been taken into account here. The peak N-atom concentrations are 6×10^{12} cm^{-3}, 1.1×10^{12} cm^{-3}, and 9.2×10^{11} cm^{-3} in the flames doped with $(CN)_2$, HCN and NH_3, respectively.

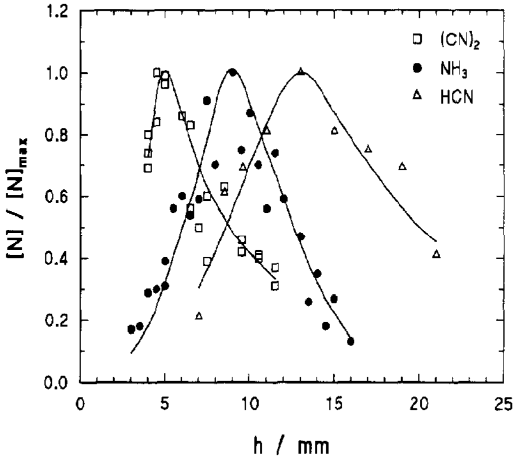

Fig. 5. N-atom concentrations in the 33 mbar flames versus height above the burner surface. For a better comparison, the profiles are scaled to a common maximum of 1.0; peak N-atom concentrations are 6×10^{12} cm^{-3}, 1.1×10^{12} cm^{-3}, and 9.2×10^{11} cm^{-3} in the flames doped with $(CN)_2$, HCN, and NH_3, respectively.

The N-atom profiles are strikingly different for the different additives, suggesting different chemical-reaction pathways in the N-atom formation and consumption. Flame model calculations including a thorough sensitivity analysis with the aim of simulating the measured N-atom concentrations are being pursued.

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