Flame temperature measurement using picosecond transient grating experiments

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Picosecond transient grating experiments were performed on a sodium-seeded methane/air flame at very small fringe spacings (<1 μm). At these fringe spacings, the grating signal decay occurs on a time scale fast compared to that of velocity changing collisions. The form of the decay is determined by the Maxwell–Boltzmann velocity distribution of the Na atoms. The data is fit with one adjustable parameter, the temperature. These experiments demonstrate a potentially useful approach for the non-invasive measurement of flame temperatures in small regions of a flame.

1. Introduction

Flames are complex chemical systems that involve hundreds of chemical reactions occurring among many species [1]. The chemical species vary in concentration with position in a flame and communicate with each other through transport and collisional processes. Knowledge of local concentrations and local flame temperatures is fundamental to understanding flame chemistry and is a necessary input for simulation of complex flame dynamics [2].

The composition and temperature of flames were initially measured using physical techniques, such as gas sampling and thermocouples. However, these methods cause significant perturbations of flame properties [3]. Physical probe methods are also limited by the hostile flame environment. Laser-based optical techniques provide non-intrusive methods for studying flame composition and temperature. Laser-induced fluorescence (LIF) [4], Rayleigh scattering [5], coherent anti-Stokes Raman spectroscopy (CARS) [6] and frequency-domain four-wave mixing [7] have been successfully employed.

Here we report results of small fringe spacing, subnanosecond transient grating (TG) experiments that examine combustion at atmospheric pressure without the influence of velocity changing collisions. The measurements demonstrate the possibility of directly determining the velocity distribution of species in flames, and thereby determining local temperatures.

2. Experimental methods

Previously, TG temperature measurements were demonstrated using a low pressure cell of sodium vapor [8]. Under collision free conditions, the grating signal decay is the Fourier transform of the Maxwell–Boltzmann velocity distribution, i.e. a Gaussian. Such a decay was observed, and the grating temperature determined was the same as the sample cell temperature. Here the method is extended to flames.

The TG [9] is a time-domain four-wave mixing technique in which two time-coincident excitation pulses of wavelength λ are crossed at an angle θ to form an interference pattern of fringe spacing

$$d=\lambda/[2\sin(\tfrac{1}{2}\theta)]\,. \qquad (1)$$

In the experiments described here, the excitation beams are resonant with a Na electronic transition, so the interference pattern creates a spatially periodic variation in the Na electronic-state populations. This periodic variation in turn acts as a diffraction grating for a probe pulse that is brought in some time

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later at the grating Bragg angle. The intensity of the diffracted signal is recorded as a function of the delay between creating and probing the grating.

The signal decays as Na atoms move between grating peaks and nulls; thus, the distance scale in a TG experiment is the peak-null separation, $\frac{1}{2}d$. If $\frac{1}{2}d$ is less than the Na mean free path, the Na-transport contribution to the grating decay is essentially free of the effects of velocity-changing collisions. The grating decay is then a probe of the Maxwell–Boltzmann velocity distribution of the Na atoms [10], and thus provides a means for measuring the translational temperature in the beam-crossing region.

The excitation and probe pulses are generated by two independently tunable, cavity-dumped dye lasers pumped by a frequency doubled, Q-switched and mode-locked Nd:YAG laser operated at 1 kHz. The excitation laser was tuned to the 589.0 nm, Na D1 transition ($3S$–$3P_{1/2}$). The probe laser was tuned to the 568.8 nm, $3P_{3/2}$–$4S$ transition. The dye lasers produce 25 ps, 10 μJ pulses. A computer controlled optical delay line temporally delayed the probe pulse. The beams were focused to spot sizes of 200 μm and attenuated to 100 nJ before entering the flame. A cooled photomultiplier tube was used to detect the diffracted signal. The phototube output was sent to a gated integrator. The computer that controlled the delay line also recorded the output of the gated integrator to yield curves of the signal amplitude versus delay.

The flame burned a lean CH_4/air mixture with a fuel/oxidant equivalence ratio of 0.8. A 0.26 M solution of NaCl was pumped into the analytical burner at 1.1 ml/min. The beams intersected 3 mm above the flame front, which was 13 mm above the slot of the burner. To measure reproducibly the same spot in the flame at different fringe spacings a metal plate holding a pin hole was machined to fit into the burner slot. The pin hole could be repositioned relative to the burner slot to within a few μm. The excitation and probe beams were crossed through the pin hole, the metal plate was removed, and the flame was turned on. The flame was allowed to stabilize for at least 15 min before measurements were made. To change fringe spacings, the flame was turned off, the plate was placed in the slot, the angle between the beams was changed, and the beams were again crossed through the pin hole.

3. Results and discussion

Many of the considerations relating to picosecond TG experiments in low pressure gases and flames have been discussed previously [10,11]. Collision and diffusion effects have been investigated for this flame system [11]. Large fringe spacings were used in these earlier studies such that velocity changing collisions were important and transport was diffusive. Here the fringe spacings are small, so transport free of velocity changing collisions makes the major contribution to the grating decay. In the absence of all other processes, a Maxwell–Boltzmann velocity distribution will make the signal decay as [10],

$$S(t) = A \exp[-(\Delta t)^2 k_B T/m] , \qquad (2)$$

where the grating wave vector, $\Delta = 2\pi/d$; k_B is the Boltzmann constant; m is the mass of the Na atom, and T is the translational temperature. Since Δ and m are known, T can be obtained from the data.

In the actual experiments, two more factors influence the decay. The first is the decay of the grating by relaxation to the ground state, which is taken into account by multiplying the right-hand side of eq. (2) by $\exp(-2t/\tau)$, where τ is the excited-state lifetime. The second arises because the first excited state of Na is split into a 17 cm^{-1} doublet by spin–orbit coupling. At flame temperatures, the populations of the two spin–orbit states equilibrate quickly after optical excitation. In our experimental procedure, the lower-energy spin–orbit state is excited, and a transition from the upper state of the doublet to a higher-lying excited state is probed. Thus, the signal grows in with the rate of scattering between the spin–orbit states and decays due to the translational motion of the atoms. Exciting and probing the same transition (or a transition with a level common to excitation and probing) results in a large coherence spike, due to the macroscopic polarization that is initially produced upon excitation. Because the pulses used in these measurements are relatively long, the coherence spike masks the relevant data. The excitation and probing scheme used here eliminates the coherence spike.

When the lifetime decay and the scattering between the spin–orbit levels are included, the expression for the signal becomes,

$$S(t)=A\exp(-2t/\tau)\,[1-\exp(-k_s t)]^2 \times\exp[-(\Delta t)^2 k_B T/m]\,. \quad (3)$$

k_s is the rate constant for scattering between the spin–orbit states. Both k_s and τ have been measured previously [11]. In the flame studied here, τ is dominated by collisional quenching rather than the radiative lifetime [11].

Eq. (3) was derived without considering the influence on the velocity distribution of the scattering events that populate the upper spin–orbit state. The rate of a scattering process in a flame can be used to obtain the scattering cross section, but the average mass of the scattering species introduces a modest element of uncertainty. For population-quenching or population-scattering collisions, the relative population of potential scattering partners may also be an unknown, and therefore it may be possible only to calculate a minimum scattering cross section. We have used TG measurements to calculate the scattering cross section for velocity changing collisions as well as the minimum cross section for quenching the excited-state population-scattering in several premixed, Na-seeded flames [11]. The calculated diffusional (velocity-changing) collision cross sections were within experimental error of the minimum quenching cross sections and were smaller than the minimum excited-state population-scattering cross sections, even when the major constituent of the flame was argon (which is an inefficient quencher of Na excited states). The actual cross sections for quenching and excited-state population-scattering must therefore be significantly larger than the velocity-changing collision cross section. This implies that collisions that scatter excited-state population between spin–orbit states can occur with little or no change in the Na velocity. A grazing collision can easily transfer 17 cm^{-1} of energy between the Na P states and the rotational modes of a polyatomic flame molecule. In fact, even if all of the energy were to go into translational modes, 17 cm^{-1} is vastly smaller than kT at flame temperatures. Thus it is quite reasonable to assume that the excited-state population-scattering collisions that make this probing scheme possible have little effect on the overall Na velocity distribution. This is tested by performing the experiments at several small fringe spacings.

Fig. 1 displays calculations showing the sensitivity of the grating decay to the temperature. In fig. 1, eq. (3) is plotted for several temperatures (1600, 1800, and 2000 K), a 0.5 μm fringe spacing, and the mass of Na. The values for τ (800 ps) and k_s (1.6×10^9/s) are those obtained from measurements at large fringe spacings [11]. Fig. 1 illustrates the importance of including the actual dynamics of the system under investigation in the analysis, and demonstrates that, in spite of the population kinetics, there is information on the flame temperature.

Fig. 2 shows the grating decay for one data set taken at a fringe spacing of 0.45 μm, and a fit using eq. (3). The temperature is the only unknown; the other parameters are the same as those used for fig. 1. In analyzing the data, the influence of the ≈25 ps laser pulse shape, obtained by measuring the grating signal from a sample of liquid CS_2 [12], was included in the analysis. The pulses can be accurately modeled as a double-sided exponential. To calculate the data, eq. (3) is convolved with the pulse shape; the result is squared, and again convolved with the pulse shape [13]. The critical placement of $t=0$ for the convolution is determined from the peak of the CS_2 signal.

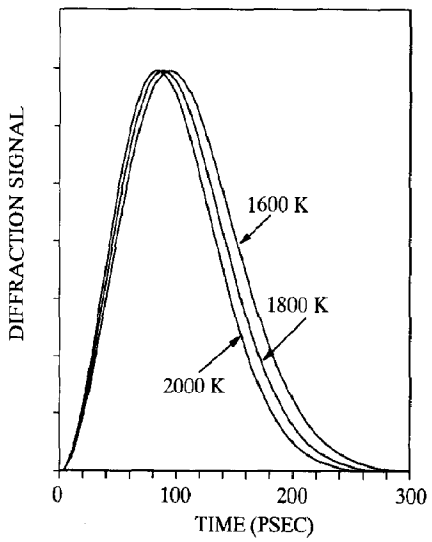

Fig. 1. Plots of eq. (3) at 1600, 1800, and 2000 K, a fringe spacing of 0.5 μm, and the mass of the Na atom.

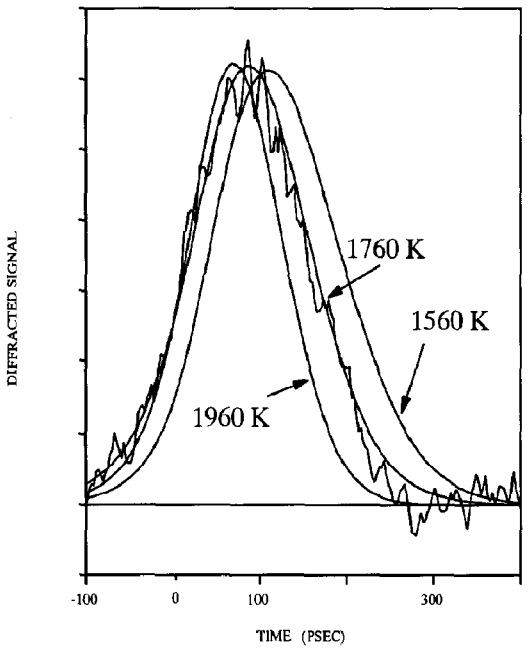

Fig. 2. TG data taken on Na in a lean methane/air flame at fringe spacing of 0.45 μm. The data is fit using eq. (3), yielding a flame temperature of 1760 K. Two other calculated curves are shown for temperatures 1560 and 1960 K. These curves show the sensitivity of the measurement to the temperature.

Accurate convolution is necessary because the laser pulses used in these experiments were relatively long. The temperature from this data set is found to be 1760 K. Also shown on fig. 2 are two other calculated curves for temperatures 1560 and 1960 K. These curves demonstrate the sensitivity of the data to the temperature. Data were taken with four other small fringe spacings, and several data sets were taken at each fringe spacing. The distance scale associated with the measurement is $\frac{1}{2}d$, or 0.2 to 0.3 μm. If velocity-changing collisions were important on this distance scale, then they would become more important as the fringe spacing is increased. For large enough fringe spacing (several μm), transport is diffusive [11], and the decays become slow. Table 1 shows the average measured temperature of all data sets taken at a given fringe spacing. For the small fringe spacings used here, there is no systematic change in the results as the fringe spacing is increased. This supports the proposition that velocity-changing collisions are unimportant in the analysis of these data.

Table 1
Temperatures measured at several fringe spacings

Fringe spacing (μm)	Measured temperature (K)
0.45	1690
0.49	1760
0.53	1690
0.55	1590
0.59	1720

The average of all data sets taken at several small fringe spacings gives a flame temperature of 1730 ± 200 K. LIF, CARS, and absorption experiments have measured the methane/air flame temperature to be 2000 K for a stoichiometric mixture [4]; the adiabatic flame temperature for such a mixture is 2200 K. A lean methane/air flame such as ours with an equivalence ratio of 0.82 was found to burn at a much reduced temperature of about 1800 K [14]. In addition, the water present in the mixture will reduce the flame temperature compared to a pure methane/air flame [15]. Therefore, the temperature measured here with the TG technique is consistent with previous measurements.

It should be possible to improve greatly the quality of TG flame temperature measurements. The most serious drawback of the system employed to do these experiments is the long pulse durations. The calculations shown in fig. 1 do not include convolutions; when convolutions are included, the separations between curves for different temperatures are reduced. Furthermore, determining $t=0$ is extremely important in determining the flame temperature. For a ≈ 25 ps pulse, this can only be determined to ≈ 10 ps. Using 2 to 4 ps pulses would eliminate this problem. Furthermore, the experiments were conducted with ≈ 100 nJ pulses at 1 KHz repetition rate. These experiments could be conducted at 4 MHz using a pair of cw mode-locked YAG- or YLF-pumped, cavity-dumped dye lasers. The high repetition rate would make it possible to eliminate a substantial amount of noise caused by fluctuations in the flame. We estimate that the combination of short pulses and high repetition rate would make it possible to determine flame temperatures using Na as a probe to within ± 50 K or possibly better.

4. Concluding remarks

We have demonstrated in principle the ability of picosecond, small fringe-spacing grating experiments to measure non-invasively the local velocity distribution (and therefore the local translational temperature) of flame species. The experiments examined Na-seeded flames. In some situations of practical importance, it might be possible to seed Na into a flame as a temperature probe. In addition, Na is naturally occurring in coal. However, it should be possible to do the same type of experiment on species that are intrinsic to flames, e.g., OH radical. In any system there will undoubtedly be dynamics other than transport of the species of interest that influence the time dependence of the grating signal. By making grating measurements at large fringe spacings, the dynamics other than transport can be observed, and thus removed from the small fringe spacing decays used to measure temperature.

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