Picosecond time-resolved four-wave mixing experiments in sodium-seeded flames

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Received September 17, 1990; accepted November 12, 1990

Picosecond four-wave mixing experiments have been used to study collisions in a Na-seeded, premixed, methane–air flame. Population gratings are used to measure Na excited-state quenching collision rates, while polarization gratings are used to measure Na ground-state hyperfine coherence randomizing collision rates and overall Na diffusion rates, even though these processes are slower than the excited-state quenching rate.

The ability to probe noninvasively the local properties of flames (e.g., transport properties, species concentrations, temperature, reaction rates, and collision cross sections) over small (submillimeter) distance scales is essential to the understanding of combustion. The advent of lasers has allowed some of these processes to be studied, and techniques such as laser-induced fluorescence, Raman spectroscopy, and absorption measurements have become the mainstays of combustion research.[1] These experiments tend to be difficult to perform, however, owing to a combination of weak signals and a large amount of background noise (both from the flames and the laser beams themselves). For these reasons four-wave mixing (FWM) techniques have proved useful in combustion research; these techniques generally provide relatively strong signals that are spatially separated from the laser beams. Coherent anti-Stokes Raman spectroscopy[2] and other FWM techniques[3] have proved useful in obtaining information on steady-state flame properties such as temperature and concentration profiles. Four-, six-, and eight-wave mixing have also been used to study collision-enhanced spectra in sodium-seeded flames.[4] To study the fast-time-scale dynamics of flames (such as collisions, velocity distributions, and reactions), it is necessary to perform experiments with subnanosecond laser pulses. The picosecond transient grating[5] is a unique and powerful tool for flame research, and here we report the initial results of a study of a Na-seeded, premixed, methane–air flame.

Previous research in our laboratory has demonstrated that the transient grating is an effective method for probing velocity distributions in low-pressure gases[6] (where low pressure signifies that there are no collisions over the experimental time and distance scales). In particular, experiments were performed on Na vapor in a heated cell. Population grating decays (in which all the laser beam polarizations are parallel to one another and perpendicular to the plane of the excitation beams) give the Fourier transform of the Na velocity distribution (which is known to be a Gaussian Maxwell–Boltzmann distribution in a low-pressure gas) as predicted by theory. Surprisingly, however, polarization grating decays (in which the excitation beams are cross polarized), although having an envelope corresponding to the population grating decays, show large beats at both the ground-state hyperfine level splitting (in all cases) and the excited-state hyperfine level splittings (when the same D line is excited and probed). A theory was developed that explains these beats qualitatively as arising from coherences created between the hyperfine levels during the excitation process. Similar hyperfine level coherences in Na vapor have been studied by other investigators using continuous-wave and long-pulse FWM.[7]

In the experiments presented here, two independently tunable dye lasers produce pulses that are approximately 40 psec in duration and have bandwidths of $\sim$0.7 cm^{-1}. The excitation laser beam is tuned such that it is resonant with one of the Na D lines. This beam is then split into two parts, which are overlapped both spatially and temporally inside the flame, creating a spatially periodic modulation of Na excited states. The spacing between the fringes in this grating is dependent on the angle between the excitation beams. The beam of the probe laser (which is also tuned to a Na D line) is delayed from the time-coincident pulses by using a mechanical delay line and diffracts off the grating that is created by the excitation beams. The resulting signal beam is spatially separate from all the laser beams. The spot sizes of the beams ($1/e$ diameter) were 180 μm for the excitation beams and 140 μm for the probe beam; the beam energies were of the order of 100 nJ. The flame used is a premixed, methane–air flame seeded with Na; the burner is a Perkin-Elmer atomic absorption burner.

The flame used in this experiment is at atmospheric pressure, so there are many collisions on the experimental time scale. Unlike those in low-pressure experiments, these decays might be expected to be dominated by collision-induced relaxation of the excited-state population to the ground state. For a population grating this is true for all but the smallest fringe spacings ($\sim$1 μm), in which transport will contribute to the decay. Figure 1(a) shows population grating data taken at a fringe spacing of 13.6 μm. The excitation laser was tuned to the $P_{3/2}$ manifold (589.0 nm), and the probe laser was tuned to the $P_{1/2}$ mani-

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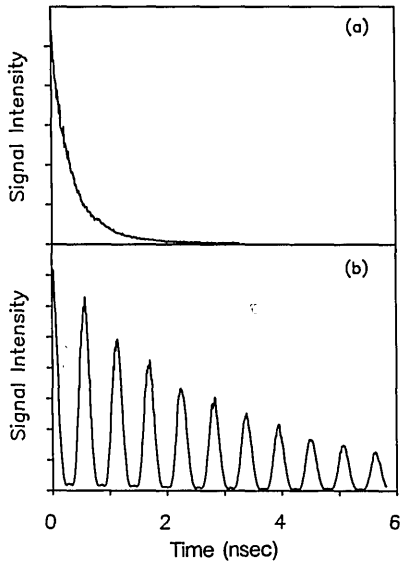

Fig. 1. (a) Population grating decay (fringe spacing 13.6 μm, λ_{exc} = 589.0 nm, λ_{probe} = 589.6 nm). (b) Polarization grating for the same fringe spacing as in (a). This decay is also exponential and shows beats at the 1.77-GHz ground-state hyperfine splitting. The decay of the polarization grating is approximately seven times slower than the population grating decay.

fold (589.6 nm). This permitted scattered light from the excitation beams to be removed with an étalon. The decay is exponential (except for coherence effects, which happen only when all three beams are time coincident at $t = 0$). The exponential decay time is 410 psec, which is much shorter than the collisionless Na lifetime of 16 nsec.[8] The decay is essentially fringe-spacing independent for large fringe spacings (>5 μm). Molecules that are effective quenchers of Na excited states [such as N_2 (Ref. 9)] are present in the flame in large quantities. If we take the flame temperature to be ~1800 K, the quenching collision cross section is of the order of 0.2 nm^2. Studies in Na–N_2 gas cells show that the cross section for collisions that scatter between the $P_{1/2}$ and $P_{3/2}$ levels is an order of magnitude greater than this[10]; thus the populations of the excited-state levels equilibrate in a time shorter than the pulse duration, and therefore this scattering does not contribute to the grating decay.

Figure 1(b) shows a polarization grating decay taken at the same fringe spacing as in Fig. 1(a). Changing the polarization of one of the excitation beams by 90° causes the data to change dramatically in two ways. First, the data exhibit beats at the ground-state hyperfine splitting frequency, as has been observed previously under collision-free conditions.[6] Second, the beats are superimposed onto an exponential decay. The decay time is 2.8 nsec at this fringe spacing; this is approximately seven times slower than the decay of the corresponding population grating. Remarkably, the decays of the excited-state population has no impact on the polarization grating signal. As is discussed in detail below, at moderate fringe spacings the polarization grating decay is determined by the diffusion of Na atoms and ground-state collisions that scramble the hyperfine levels.

To explain the effects seen in the polarization grating, we turn to perturbation theory[11] to calculate the nonlinear polarization of the Na atoms in the flame. This is a unique problem that has not been addressed in detail previously in the time domain. An initial outline of this calculation is given here.

Although 48 diagrams must be considered for a general FWM process, time ordering and resonance considerations allow us to consider only two of these processes when the probe beam is not temporally overlapped with the excitation beams. Into the population terms we incorporate the collision-induced damping constant Γ_e. These terms correspond to processes that leave atoms in superpositions of one ground state and one excited state after the excitation pulses. These atoms undergo quenching collisions at rate Γ_e before the arrival of the probe pulse. We do not include this damping constant in the ground-state Zeeman or hyperfine coherence terms (which describe superpositions between one excited-state level and two ground-state levels), as quenching into one ground-state level cannot destroy a coherence between two ground-state levels. We incorporate another damping constant, Γ_g, to account for the loss of these ground-state coherences. We make the simplifying assumption that the laser pulses are of reasonably low power and are delta functions in time, as is the signal pulse. (These assumptions do not significantly affect the calculated signals.) For excitation into the $P_{1/2}$ manifold and probing the $P_{3/2}$ manifold, we calculate a population grating signal

$$S(t) \propto \exp[-2(\Delta^2 D + \Gamma_e + 1/\tau)t], \quad (1)$$

where Δ is 2π divided by the fringe spacing, D is the Na diffusion constant, and τ is the excited-state lifetime. The polarization grating signal is given by

$$S(t) \propto [43 + 60\cos(\omega\tau) + 25\cos(2\omega\tau)] \times \exp[-2(\Delta^2 D + \Gamma_g)t], \quad (2)$$

where ω is the ground-state hyperfine splitting frequency. The numerical constants arise from the quantitative evaluation of the relevant diagrams. Note that the data do show small peaks between the large oscillations; these arise from the $\cos(2\omega\tau)$ term.

These data are essentially the Fourier transform of the high-pressure, frequency-domain data of Rothberg and Bloembergen.[7] In the frequency domain, however, collisions are required to see Zeeman and hyperfine resonances (these are termed pressure-induced extra resonances). A novel feature of this time-domain experiment is that the same resonances appear even though no collisions occur during the excitation pulses (indeed, the calculation explicitly assumes that the excitation pulses are time-coincident temporal delta functions); thus we observe extra resonances that are induced purely by the transient nature of the light fields. This is borne out by the observation of the same oscillations in the low-pressure experiment.[6]

This calculation shows that the population grating is sensitive only to processes that affect excited states, i.e., diffusion, collisional quenching, and fluorescence. The polarization grating is sensitive only to processes that affect the ground state, i.e., diffusion and decay of

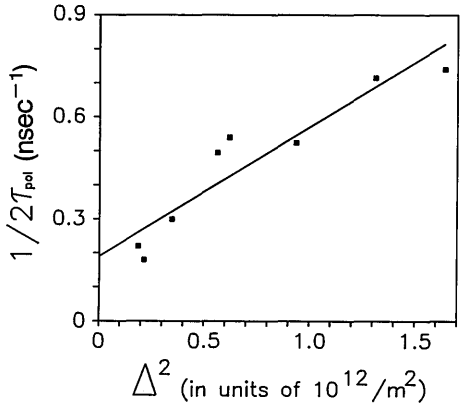

Fig. 2. Polarization grating decay constant versus Δ^2. The slope of the plot gives the Na diffusion constant D, while the intercept gives the ground-state hyperfine randomizing collision rate.

ground-state hyperfine superpositions. Thus the polarization grating is able to probe Na dynamics even after all the atoms have returned to the ground state. Note that Γ_e does not appear in the expression for the polarization grating signal.

Qualitatively, the two gratings produce signals in the following ways. The population grating generates a signal because it causes a spatially periodic depletion of the ground-state populations. As the population returns to the ground state, the signal decays. The polarization grating also causes depletion of the ground states, but this depletion is spatially uniform. The polarization of the light that causes this depletion is spatially modulated, however; it changes from right circularly polarized (rcp) to linear to left circularly polarized (lcp) to linear (of opposite polarization to the other linear region) and back to right circularly polarized over each fringe spacing. The grating signal comes from ground-state coherences produced between magnetic sublevels in the hyperfine levels; these coherences are spatially periodic because of the spatial periodicity of the lcp and rcp excitation. When the uniform excited-state population returns to the ground state, it has no influence on the ground-state hyperfine superposition grating.

Thus the population gratings decay exponentially at the quenching collision rate (which is faster than the rate at which diffusional motion causes the gratings to decay for moderate and large fringe spacings). The polarization gratings decay exponentially (with modulations) at a rate determined by ground-state randomizing collisions and diffusion. The influence of the Na diffusion is observed because the decay arising from Γ_g is relatively slow. Figure 2 is a plot of polarization grating decay constants versus Δ^2. The slope of this plot gives a D of 3.8 cm^2/sec, which is in good agreement with previous studies that make measurements over a much larger distance scale.[12] The intercept of the plot gives a ground-state hyperfine randomizing collision time of 6.5 nsec.

The real power of time-resolved transient grating experiments for studying flames, plasmas, and other complex systems lies in the fact that polarization and population gratings will measure different processes in any situation in which different transitions are driven by lcp and rcp light. In the Na-seeded flame, we are able to obtain experimentally the quenching collision and ground-state randomizing collision cross sections as well as the diffusion constant; thus this technique can readily probe the influences of different collision partners. It could be used, for example, to probe the interactions of highly reactive species present in flames. The time-resolved transient grating method promises to be useful in gas phase research and in combustion research in particular.

The authors thank Rick Trebino and Mark Dugan for helpful discussions. This research was supported by the Office of Naval Research, Physics Division. John T. Fourkas thanks the National Science Foundation for a graduate fellowship.

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