Detection of atomic hydrogen by two-color laser-induced grating spectroscopy

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We report a novel multiphoton scheme for the detection of atomic hydrogen. Interference of two laser beams near 243 nm crossed at a small angle induces a spatially modulated two-photon excitation (i.e., a grating of excited atoms), which diffracts a third laser beam tuned to either 486 or 656 nm to generate a coherent signal beam. We demonstrate the technique by making H-atom concentration measurements that compare quantitatively with those made using laser-induced fluorescence in low-pressure H_2/O_2 flames.

A variety of multiphoton excitation techniques have been developed for detecting atomic hydrogen in environments such as flames and electrical discharges that are opaque at the Lyman-α (L-α) resonance absorption wavelength. Quenching, interferences, and restricted access to these environments often limit the accuracy of multiphoton techniques such as laser-induced fluorescence[1] (LIF) and multiphoton ionization.[2] The coherent nature of other methods, such as stimulated emission,[3] third-harmonic generation,[4] and polarization spectroscopy,[5] is important because a directional signal beam is generated, but stimulated emission signals are difficult to qualify, third-harmonic generation operates at L-α, and polarization spectroscopy lacks high sensitivity. In this Letter we describe a new method for detecting atomic hydrogen, two-color laser-induced grating (LIG) spectroscopy[6] (two-photon excited and one-photon probed), which has the advantageous properties associated with a visible detection wavelength and a coherent signal beam yet retains sensitivity comparable with LIF in low-pressure, premixed flames. In addition, we derive reliable concentration measurements from LIG signals using known theory for the nonlinear susceptibility $\chi^{(5)}$ involved in this six-wave-mixing process.

Resonant wave-mixing techniques are now being investigated as combustion diagnostics for many species. Na, OH, NH, and NO have been detected in flames by using resonant degenerate four-wave mixing.[7–10] Double-resonance wave-mixing methods are also being developed as background-free alternatives to fluorescence-dip techniques.[6,11,12] Except for coherent Raman spectroscopy, there are fewer examples of wave-mixing techniques involving two-photon resonances.[13] The goals of the present research on atomic hydrogen are to demonstrate multiphoton two-color LIG spectroscopy and to investigate the applicability of LIG spectroscopy to concentration measurements in laboratory flames.

We used two Q-switched Nd:YAG-pumped dye lasers to generate LIG and LIF signals in this study. The first laser, operating near 486 nm (H-β), was frequency doubled in β-barium borate to produce 7-ns pulses having a bandwidth $\Delta\nu = 0.5$ cm^{-1} and energies of up to 1.5 mJ. The 243-nm output was split into two excitation beams having roughly equal intensity, focused by a 1000-mm lens, and crossed at a full angle (2θ) of 2° through a flame. The difference in path lengths traversed by these two beams was carefully reduced to a fraction of their pulse coherence length [$(2 \ln 2/\pi)^{0.5}/\Delta\nu \approx 1.3$ cm] so that they interfered in the overlap region (diameter $\approx$0.3 mm, length $\approx$30 mm).

The second dye laser, operating near 656 nm (H-α), formed the probe beam (7-ns pulses, $\Delta\nu \approx 0.1$ cm^{-1}). We initially used the fundamental of the first dye laser (H-β) as a probe beam for experimental simplicity (since $4\omega_{42} \sim \omega_{21}$) and obtained adequate LIG signals. Here we describe only the H-α probe studies, where pulses from the second dye laser could be timed and tuned independently from the excitation pulses because these were more informative. The H-α probe beam was attenuated to pulse energies less than 20 μJ, collimated at a diameter of 1 mm, and crossed through the excitation beams at the phase-matching angle of 5.4°. All three input beams and the resulting signal beam were in the same plane parallel to the burner surface, and the excitation and probe beams had orthogonal polarizations.

To reject stray light, we directed the LIG signal beam to a photomultiplier tube through three apertures and a H-α bandpass filter. LIF was simultaneously collected at $f/4$ through a side window of the vacuum housing and a H-α bandpass filter. The gated photomultiplier tube outputs were integrated, digitized, and averaged for 40 to 60 laser pulses. The pulse fluctuations in LIG signals were much larger than in LIF because of LIG's greater sensitivity to energy and bandwidth fluctuations in the excitation laser beams. LIG signals could be eliminated by blocking any one of the three input beams, whereas LIF signals remained after blocking either one of the excitation beams. We detected a maximum of $\sim 1 \times 10^6$ LIG and $\sim 5 \times 10^4$ LIF photons/laser pulse in a premixed H_2/O_2 flame where the peak H-atom concentration is estimated[1] as [H] $\sim 2 \times 10^{15}$ atoms/cm^3.

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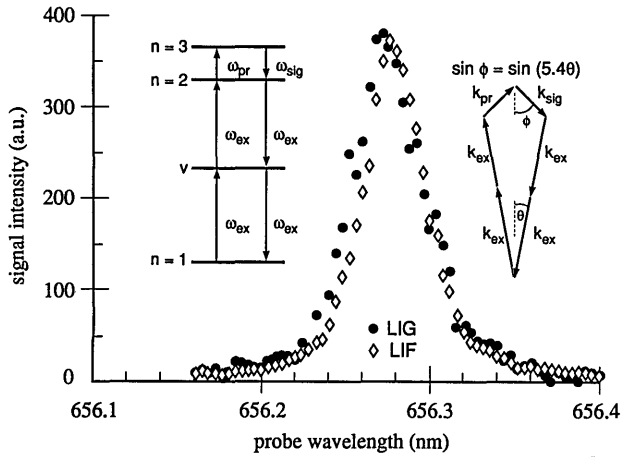

Fig. 1. Insets: energy-level and vector phase-matching diagrams for H showing the two-photon excitation (ω_{ex}), probe (ω_{pr}), and signal (ω_{sig}) transitions, including schematically a single virtual level v in place of a sum over all nonresonant states. LIF requires only one excitation beam ($n = 1 \rightarrow n - 2$), whereas LIG requires interference between two excitation beams. Observed LIG and LIF probe spectra were recorded with the excitation wavelength fixed and are broadened mainly by the strong probe intensity.

The insets in Fig. 1 show the energy-level and vector phase-matching diagrams for the two-photon excitation (ω_{ex}), probe (ω_{pr}), and signal (ω_{sig}) transitions in LIG spectroscopy (six-wave mixing) of atomic hydrogen. Because we two-photon excite using parallel polarizations, the interfering beams form a squared sinusoidal, spatially varying population of excited atoms (i.e., a strongly peaked grating). The relative polarization of the probe beam is unimportant in scattering from this population grating. Using nonlinear-optical perturbation theory,[14] we derive the peak LIG signal intensity for this process:

$$S_{\mathrm{LIG}} \propto |\chi^{(5)}|^2 \propto N_1^2(\alpha_{12})^2(\sigma_{23})^2\tau_2^2 I_{\mathrm{ex}}{}^4 I_{\mathrm{pr}} L^2 \times \mathrm{Im}[g(\delta_{\mathrm{ex}}, \Gamma_{12})]^2 |g(\delta_{\mathrm{pr}}, \Gamma_{23})|^2, \quad (1)$$

where $\chi^{(5)}$ is the fifth-order nonlinear susceptibility, N_1 is the initial atomic hydrogen density, α_{12} is the two-photon cross section at the peak of the $1 \rightarrow 2$ transition, σ_{23} is the cross section at the peak of the $2 \rightarrow 3$ transition, τ_2 is the population decay time of the $n = 2$ level, including spontaneous emission and collisional quenching, I_{ex} is the intensity of the excitation laser beam, I_{pr} is the intensity of the probe laser beam, L is the path length where the beams overlap, and $g(\delta, \Gamma) \equiv i/(1 + i\delta/\Gamma)$ is a Lorentzian line shape function in terms of the excitation-beam detuning $\delta_{\mathrm{ex}} = \omega_{12} - 2\omega_{\mathrm{ex}}$, the probe-beam detuning $\delta_{\mathrm{pr}} = \omega_{23} - \omega_{\mathrm{pr}}$, and the dephasing rates Γ_{12} and Γ_{23} of the $1 \rightarrow 2$ and $2 \rightarrow 3$ transitions.

In contrast, the peak LIF signal generated by the same laser beams is

$$S_{\mathrm{LIF}} \propto \mathrm{Im}[\chi^{(5)}] \propto N_1 \alpha_{12}\sigma_{23}\tau_2\tau_3 I_{\mathrm{ex}}{}^2 I_{\mathrm{pr}} L A_{32} \times \mathrm{Im}[g(\delta_{\mathrm{ex}}, \Gamma_{12})]\mathrm{Im}[g(\delta_{\mathrm{pr}}, \Gamma_{23})], \quad (2)$$

where τ_3 is the population decay time of the $n = 3$ level, A_{32} is the spontaneous emission rate, and the excitation and probe steps are considered incoherent. Compared with LIF, the LIG signal has higher-order dependencies on many parameters yet has the same dependence on I_{pr} and on the probe line shape function because $|g(\delta, \Gamma)|^2 = \mathrm{Im}[g(\delta, \Gamma)]$. Also, the LIF signal is sensitive to τ_3 (and hence to quenching of both $n = 2$ and $n = 3$), while the LIG signal is independent of τ_3, except in its dependence on Γ_{23}. Relations (1) and (2) do not contain saturation effects.

The fringe spacing Λ of a laser-induced grating is given by[15] $\Lambda = \lambda_{\mathrm{ex}}/(2 \sin \theta)$ for a crossing half-angle θ of the excitation beams, resulting in $\Lambda = 8$ μm for our experiments. The lifetime of a grating depends on thermal motion in addition to the decay time τ_2 from relation (1). Rose *et al.*[16] have developed a theory for these effects on normal sinusoidal gratings. This theory slightly overestimates the decay time for our case of a more strongly peaked grating; nevertheless, it yields a grating decay time of $\tau_m \approx 0.4$ ns for translational motion of H at flame temperatures in the limit where the mean free path d is much larger than Λ. The actual grating lifetime in a 30-Torr flame at 1600 K is difficult to estimate because $d \sim \Lambda$ and $\tau_2 \approx 0.5$ ns. At higher pressures, τ_2 should dominate the grating lifetime because the quenching rate increases while the motional decay rate, which becomes controlled by molecular diffusion, decreases with pressure.

We recorded LIG and LIF spectra in 30-Torr H_2/O_2 flames, shown in Fig. 1, by scanning the probe laser wavelength with the excitation laser fixed at the center wavelength of the two-photon transition. Both line shapes are described by a Voigt profile including the (Gaussian) laser bandwidths and power broadening due to the probe laser ($I_{\mathrm{sat}} < 1$ μJ). The bandwidth of the excitation laser selects ~1/3 of the velocity distribution since the Doppler width is 1.3 cm^{-1} for H at 1600 K excited near 243 nm. Our LIG spectra do not contain a nonresonant background or any noticeable asymmetry, as are often observed in coherent anti-stokes Raman spectroscopy. A thermal grating, which may form as a result of quenching of two-photon-excited atoms, thus apparently diffracts the probe beam much less efficiently than an $n = 2$ population grating. However, LIG spectra are shifted slightly (0.1 cm^{-1}) relative to LIF, and this unexplained shift persists

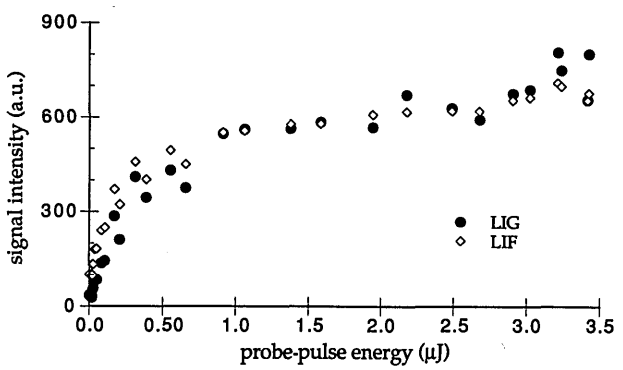

Fig. 2. Observed LIG and LIF signals in atomic hydrogen saturate comparably with increasing probe intensity while yielding similar line shapes (see Fig. 1).

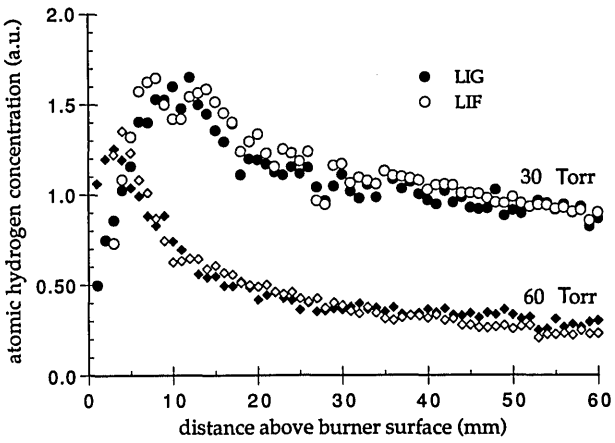

Fig. 3. Atomic hydrogen concentration profiles of slightly rich ($\phi = 1.2$) H_2/O_2 flames as determined simultaneously from integrated LIG and LIF signal intensities at two different pressures (same scale). The concentration is proportional to the square root of the LIG signal.

when the excitation laser is detuned to either side of the $1 \rightarrow 2$ transition.

Figure 2 demonstrates that LIG and LIF signals have a similar dependence on I_{pr} as predicted by relations (1) and (2), and LIG and LIF spectra are likewise power broadened to the same extent at high probe intensity. We also observed a very different dependence on I_{ex} for the LIG and LIF signals: $S_{LIG} \sim I_{ex}^{3.9\pm0.5}$ and $S_{LIF} \sim I_{ex}^{1.8\pm0.4}$. These results agree with relations (1) and (2) within experimental uncertainty and suggest that the two-photon excitation is not saturated at energies below 1.5 mJ. To confirm the predicted grating lifetime of $\tau < 1$ ns, we delayed the probe relative to the excitation pulse and observed LIG (or LIF) signals only when the pulses were overlapped in time. Long-lived optical gratings, which might be due to density modulation or the formation of ions, are apparently not important in two-color LIG spectroscopy applied to atomic hydrogen in low-pressure flames.

We used the LIG and LIF signals to record spatial profiles of atomic hydrogen concentration (N_1) in flat H_2/O_2 flames at pressures between 30 and 90 Torr and equivalence ratios between $\phi = 0.8$ and $\phi = 1.5$. We normalize the LIG and LIF signals for variations in laser intensity according to relations (1) and (2) and then compare relative concentrations, seen in Fig. 3, noting that $N_1 \propto (S_{LIG})^{0.5}$. In general, the profiles are quite comparable for different flame pressures and stoichiometry. The resonantly detected LIF signal is less reliable near the burner because of scattering by the probe beam at the surface. On the other hand, the LIG signal is sensitive to optical alignment, requiring more care for making reliable intensity measurements.

In summary, the spectral, temporal, and intensity observations described here for LIG spectroscopy of atomic hydrogen all indicate that an $n = 2$ population grating is the primary mechanism producing a coherent signal at pressures below 90 Torr. Quenching is a major relaxation mechanism for this type of grating at pressures of 30 Torr and above. As a result, H-atom concentration profiles derived from LIG and LIF signals should be comparable over a range of foreign-gas pressures. LIG spectroscopy appears to have advantages over LIF when LIF measurements have limited optical access or when there are optical interferences at the detection wavelength. The sensitivity of two-color LIG spectroscopy in our low-pressure flames suggests that the method is most useful at concentrations of $[H] > 10^{13}$ atoms/cm^3.

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