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IMAGING RADICAL SPECIES IN REACTING FLOWS USING PICOSECOND TWO-PHOTON LASER-INDUCED FLUORESCENCE SPECTROSCOPY

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Introduction

A critical aspect to our evolving understanding of combustion is derived from the measurement of certain key radical species. Spatially resolved concentration measurements can provide scientific insight and can be used in combustion model development and validation studies. Key radical species can drive the combustion chemistry or their presence can indicate activation of a particular chemical pathway. Laser-induced fluorescence (LIF) imaging has been used extensively for detection of species including OH, NO, and CH, providing the high sensitivity and spatial resolution necessary for application in combustion systems.[1-3] In these cases, strong electronic transitions are accessible in the ultraviolet (UV) or visible part of the spectrum. Other fluorescent radicals, including CO and atomic species such as O and H, cannot be excited via single-photon absorption in the UV or visible because their ground-state transitions lie in the vacuum UV, where most practical systems are optically thick. In these cases, two-photon-resonant absorption of UV photons can be used to excite the fluorescence.[2,3]

The transition probabilities for two-photon resonant absorption transitions are relatively small compared to single-photon transitions, and the two-photon-resonant excitation rate scales quadratically with the laser intensity. In practice, therefore, two-photon excitation requires very high laser intensity, which can cause interference via undesirable photolytic processes in the combustion environment, including laser-induced fluorescence interference from other molecules in the sample as well as photolytic production of the target radical. In cases where the interference results from a single-photon process, it may be advantageous to use picosecond laser excitation instead of nanosecond laser excitation. To produce the same LIF signal level, picosecond excitation requires significantly less pulse energy than is necessary with nanosecond excitation. Reduced laser pulse energy generates less interference from single-photon photolysis processes.

In this paper, we review briefly two-photon excitation schemes used for LIF detection of O, CO, and H. We summarize our previous work on picosecond LIF detection of atomic oxygen, which demonstrates advantages of picosecond excitation for imaging of atomic oxygen in flames, and we discuss potential advantages for picosecond two-photon imaging of CO and H.

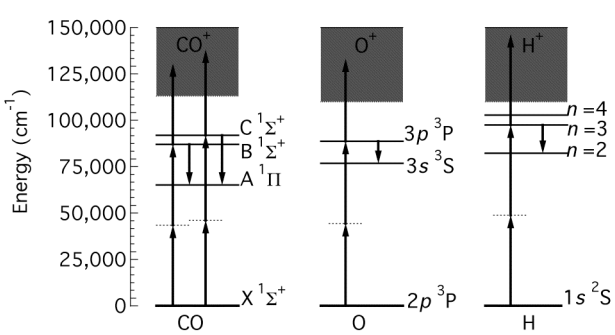

Figure 1. Two-photon excitation schemes for CO, O, and H.

Discussion

Two-photon-resonant LIF schemes for atomic oxygen, carbon monoxide, and atomic hydrogen are shown in Fig. 1. The following subsections address each scheme individually.

Atomic Oxygen. Atomic oxygen is a critical combustion intermediate, but its detection in flames has remained elusive. Two photons at 226 nm excite ground-state atomic oxygen via the 3p 3P←←2p 3P transition, and fluorescence is detected from the 3p 3P→3s 3S transition at 845 nm. Two-photon LIF detection of atomic oxygen requires UV pulses of sufficiently high energies that flame measurements are often plagued by photolytic production of atomic oxygen.[4-8] Evidence of atomic oxygen production through rapid dissociation after excitation of the O_2 Schumann-Runge bands was observed in lean H_2/O_2 flames.[4] Hydrocarbon flames, however, represent a considerably more complex system, and early experiments observed additional photochemical interferences occur in hydrocarbon flames, especially for fuel-rich conditions.[6,9,10] Investigators had speculated on potentially important precursor molecules, suggesting that CO or CH_2O may contribute to the photolytic signal, but no direct evidence had been presented previously.[9,10] In a recent experiments we characterized the photolytic production of atomic oxygen in diffusion[11] and premixed flames.[12] Our pump-probe experiments strongly implicate a single-photon photodissociation of vibrationally excited CO_2.

We investigated photolytic production of atomic oxygen using a weak picosecond probe laser to measure relative oxygen atom concentrations in a well-characterized laminar CH_4/air diffusion flame.[11] The measured ps-LIF profile of atomic oxygen agreed very well with a numerically simulated profile. Subsequently, we showed that an intense nanosecond photolysis laser generated oxygen atom concentrations of the same order of magnitude as the naturally occurring concentrations. Photolytic production of atomic oxygen depended linearly on the photolysis laser pulse energy, indicative of a single-photon photolysis process. By scanning the wavelength of the photolysis laser it was shown that absorption spectrum of the precursor molecule did not exhibit a discrete-line structure around 226 nm. In particular, photolysis of O_2 via Schumann-Runge transitions was shown to be negligible. This finding is, however, consistent with the UV absorption spectrum of CO_2, which is broad and featureless.[13] Using the measured temperature, the calculated CO_2 concentration, and the measured CO_2 absorption cross section,[13] we simulated the laser-excited CO_2 profile and demonstrated excellent agreement with the measured profile of photolytically produced oxygen atom. All of these results are consistent with vibrationally excited CO_2 being the photolytic precursor molecule responsible for atomic oxygen production at 226 nm in a CH_4/air diffusion flame.

Subsequent experiments using 1-D line imaging of atomic oxygen confirmed this finding in premixed CH_4 flames. A significant increase in photolytic production of O was observed when the CO_2 concentration in the flame was increased, and insignificant photolytic production of O was observed in a hydrogen-fueled flame containing no CO_2. Results demonstrated ps-LIF signals were more than an order of magnitude larger than ns-LIF signals when the photolytic interference was comparable in the two cases.[12]

Thorough characterization of the photolytic interference enabled the design of 2-D imaging experiments that ensured photolytic contributions to the signal were at the level of the measurement noise. Using excitation with 50-ps laser pulses, we successfully demonstrated interference-free, 2-D imaging of atomic oxygen in a laminar flame[12] and in a flow-flame interaction experiment.[14]

Carbon Monoxide. Two-photon-resonant LIF detection of CO has received considerable attention for applications in combustion (see, for example, the references listed in Ref. 15). The technique

employs two-photon excitation of the Hopfield-Birge electronic transition ($B\ ^1\Sigma^+ \leftarrow\leftarrow X\ ^1\Sigma^+$) at 230 nm and collection of the blue-to-green emission in the Angström bands ($B\ ^1\Sigma^+ \rightarrow A\ ^1\Pi$). As in the detection of atomic oxygen with excitation at 226 nm, photodissociation of vibrationally excited CO_2 can cause interference to the measurement of CO using excitation at 230 nm.[16] Because the CO_2 absorption cross section increases with decreasing wavelength,[13] we expect increased interference from photolytic production of CO in the $C\ ^1\Sigma^+ \leftarrow\leftarrow X\ ^1\Sigma^+$ excitation scheme at 217 nm.[17]

Photolytic production of CO results in more significant measurement interference as the ratio of the CO concentration to the CO_2 concentration decreases. CO detection in rich flames, where CO concentration is high, may not suffer significantly from photolytic interference. The detection of CO in lean flames, however, can be compromised significantly by photolytic interference because the CO concentration is very low compared to that of vibrationally hot CO_2. In this case, we expect that picosecond excitation may enable significantly improved interference-free detection limits.

Atomic Hydrogen. Laser-induced fluorescence detection of atomic hydrogen is possible using a variety of multi-photon excitation and detection schemes. Czarnetzki *et al.*[18] compare different schemes employing multi-photon excitation to the n=3 and n=4 levels and subsequent detection of the Balmer-line fluorescence. In the current work, we focus on the simplest scheme, using two-photon excitation at 205 nm to excite hydrogen atoms n=3 levels.[19] Subsequent Balmer-α fluorescence is detected at 656 nm. Although this scheme may be particularly prone to photolytic interference, it is the simplest scheme to implement for multi-photon LIF imaging because it involves a single laser pulse and requires less complicated corrections for spatial variations in the laser sheet(s) than the other multi-color schemes.

Detection of atomic hydrogen in flames is plagued by photolytic interference. One of the reasons that prior investigators used more complex excitation schemes than that discussed here was to reduce photolytic interference. The observed interference has been attributed to photodissociation of H_2O [20] and CH_3 [21] at 205 nm. As we demonstrated with two-photon ps-LIF detection of atomic oxygen, picosecond excitation will reduce the interference due to single-photon photolysis by enabling the use of reduced laser energy compared to nanaosecond excitation. We are assessing improvement offered by picosecond H-atom imaging using the same approach we used in our development of two-photon ps-LIF detection of atomic oxygen to characterize the interference(s).[12]

Conclusions

Two-photon laser-induced fluorescence can be used for spatially resolved detection of O, CO, and H. Two-photon-resonant absorption requires sufficiently high laser pulse intensity that these techniques are frequently hindered by the photolytic interferences when applied in combustion systems. The interference results from photolytic production of the target molecule or atom and/or from the production of interfering fluorescence from other molecules in the sample. In cases where the photolytic interference proceeds via a single-photon process, such that it scales linearly with the laser pulse energy, it may be advantageous to use picosecond laser excitation as opposed to the more conventional nanosecond laser excitation.

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