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FREE RADICAL SPECTROSCOPY USING THE $LiCaAlF_6:Ce^{3+}$ LASER

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Abstract

Free radicals of importance to combustion processes, namely hydroxyl (OH) and methoxy (CH_3O), have been laser excited and spectroscopically characterized using the $LiCaAlF_6:Ce^{3+}$-based tunable solid-state laser.

Introduction

The laser-induced fluorescence (LIF) technique is a sensitive and noninvasive technique for imaging of flames and for monitoring of temperature and the presence of transient molecular species in flames.[1,2] Well-characterized free radicals, namely hydroxyl (OH) and methoxy (CH_3O), have convenient absorption bands that can be laser-excited in the 280-298 nm spectral region with the newly developed solid-state tunable laser based on the $LiCaAlF_6:Ce^{3+}$ (abbreviated LiCAF:Ce) single crystal[3] pumped by the fourth harmonic (266 nm) output of a Q-switched Nd:YAG laser. The chief factor governing the design of a compact solid-state tunable UV laser for LIF excitation is an appropriate choice of "pumping source - active medium" combination in order to (a) avoid complications and minimize energy consumption relating to the dye solution circulation and the concomitant photochemical instability, (b) use the same laser source efficiently for photolysis of the free radical precursor as well as for pumping the active medium, and (c) achieve a high "wall-plug" conversion efficiency for the laser unit.

The advantages of the LiCAF:Ce laser system for LIF-based free radical spectroscopy can be summarized as follows : (a) The LiCAF:Ce crystal is photochemically stable[4] and very efficient (up to 30 % slope efficiency);[5] (b) Its available tunability (281-297 nm)[3] covers the region of excitation of OH and CH_3O radicals; (c) The fourth harmonic (@ 266 nm) of the Nd:YAG laser is an efficient photolyzer of the precursors of the radicals (e.g. H_2O and CH_3ONO, respectively) and at the same time can be used for pumping the LiCAF:Ce crystal; and (d) The LiCAF:Ce laser is an-solid-state UV tunable device with direct pumping so that the laser module can be self-contained and compact.

We have successfully demonstrated a prototypical LiCAF:Ce laser system (pulse-repetition rate of 10 Hz and output spectral bandwidth of 0.15 cm^{-1}) for detection and spectroscopic characterization of the OH and CH_3O radicals.

Experimental

The fourth harmonic (266 nm; 10 mJ/pulse) of a Q-switched Nd:YAG laser [Quanta Ray GCR-11] was split into two beams of about equal intensity. One portion of the beam was used for photolysis of the free radical precursor (e.g. CH_3ONO for CH_3O and H_2O for OH) and the remainder utilized for pumping the laser crystal as shown in Fig.1. An optical scheme with counterpropagating photolysis and excitation beams traversing the chamber containing the free radical precursor was employed. Tunability of the LiCAF:Ce laser was provided by a step-motor-driven Littrow-mounted diffraction grating as indicated in Fig.2. The LiCAF:Ce tunable laser output had a spectral bandwidth of 0.15 cm^{-1} and the speed of the spectral scanning was 0.5 nm/min. Pulse repetition rate of the computer-controlled device was 10 Hz.

Results

The laser-induced fluorescence technique has high sensitivity for free radical detection and monitoring. For example, as noted by Crosley,[1] in an atmospheric pressure flame under favorable conditions the OH radical can be detected at sub-parts-per-billion concentration levels with 1 mm^3 spatial resolution, together with a temporal resolution of 10 ns. The hydroxyl radical is an important species for combustion phenomena and at the same time it is convenient for study in a flame environment because its spectrum can be easily excited and characterized.[6] In addition to the hydroxyl radical, the methoxy (CH_3O) radical has also been well-described theoretically and experimentally and is a good subject for combustion modeling. Both of these transient molecular species have analytically convenient excitation bands located in the near UV spectral region. Fig. 3. shows a representative laser excitation spectrum of the OH radical recorded with the solid state LiCAF:Ce laser system in the 32380 - 32450 cm^{-1} region both in a flame environment and in a static cell. In addition, Fig. 4. represents a typical excitation spectrum of the CH_3O radical in the spectral region 291.5 - 296.5 nm obtained with the same laser.

Thus, our laboratory experiments show that a solid state tunable UV laser based on the LiCAF:Ce single crystal pumped by the quadrupled output of a Q-switched Nd:YAG laser can be used successfully to probe free radicals of importance to combustion phenomena and also to record good quality laser excitation spectra of these transient molecular species. These considerations have been incorporated into the design of a portable tunable UV laser for laser-induced fluorescence excitation of free radicals in flames under normal as well as microgravity conditions.

Acknowledgment

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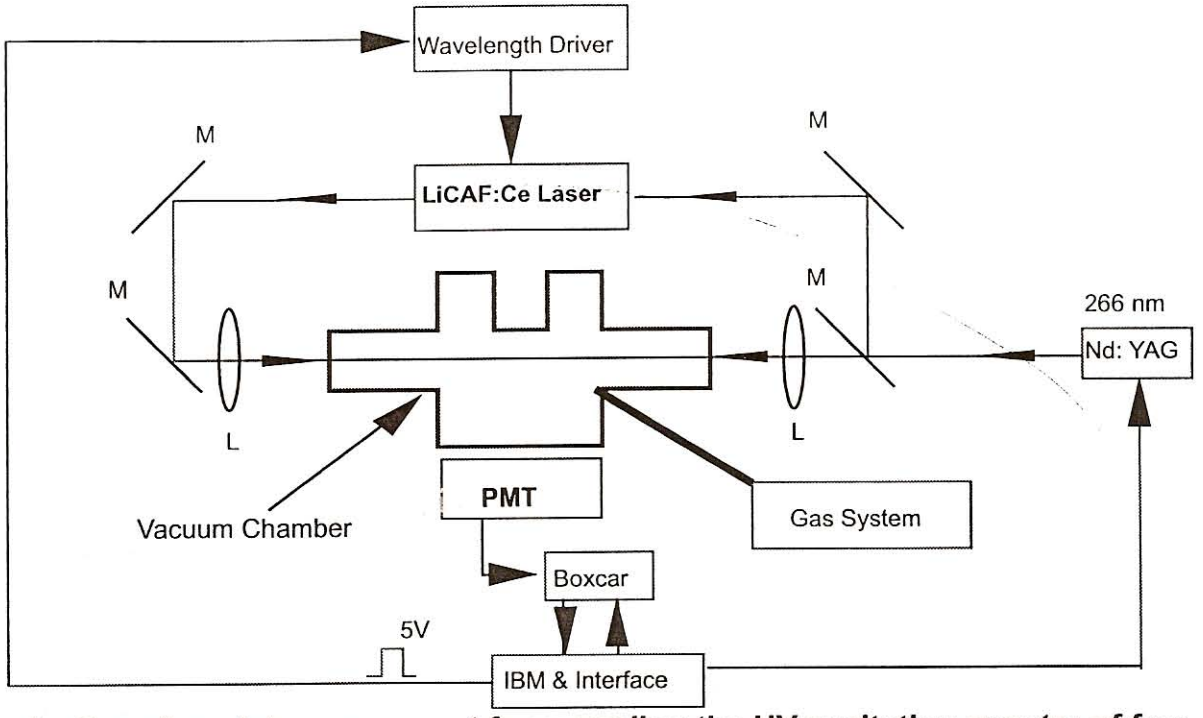

Fig 1. Experimental arrangement for recording the UV excitation spectra of free radicals using a tunable all-solid-state LiCAF:Ce laser.

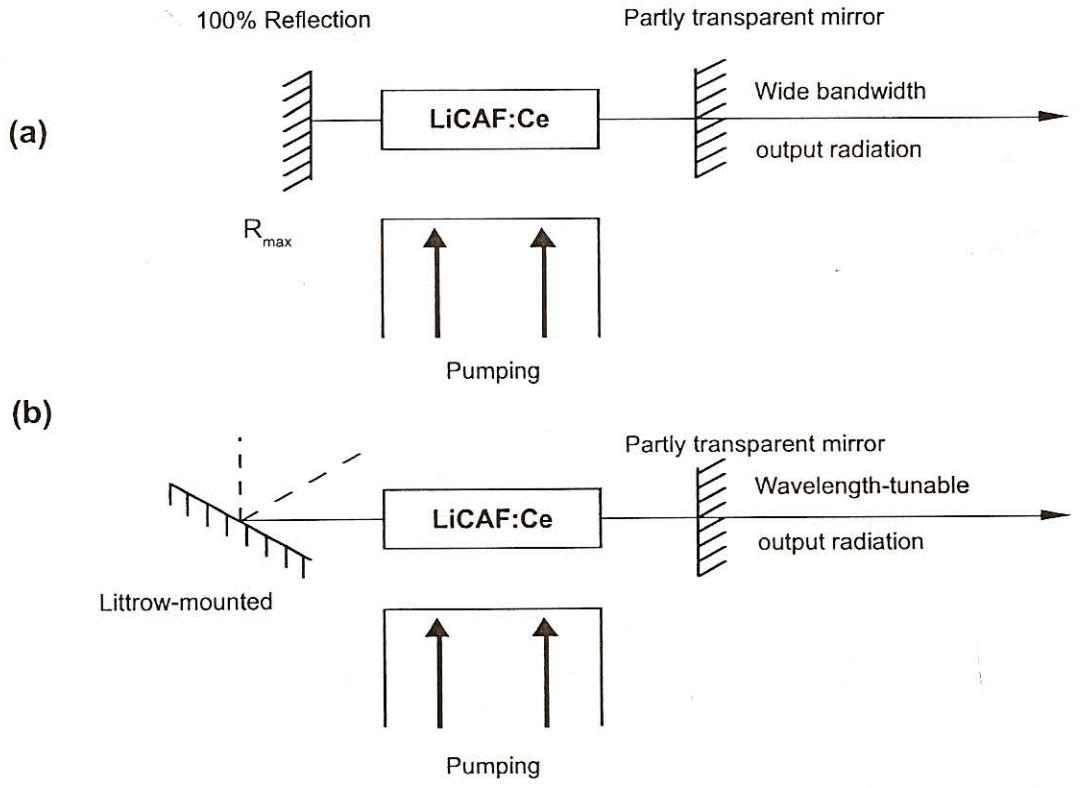

Fig 2. (a) A LiCAF:Ce laser using mirrors to form a nonselective cavity.
(b) A tunable LiCAF:Ce laser using a Littrow-mounted diffraction grating.

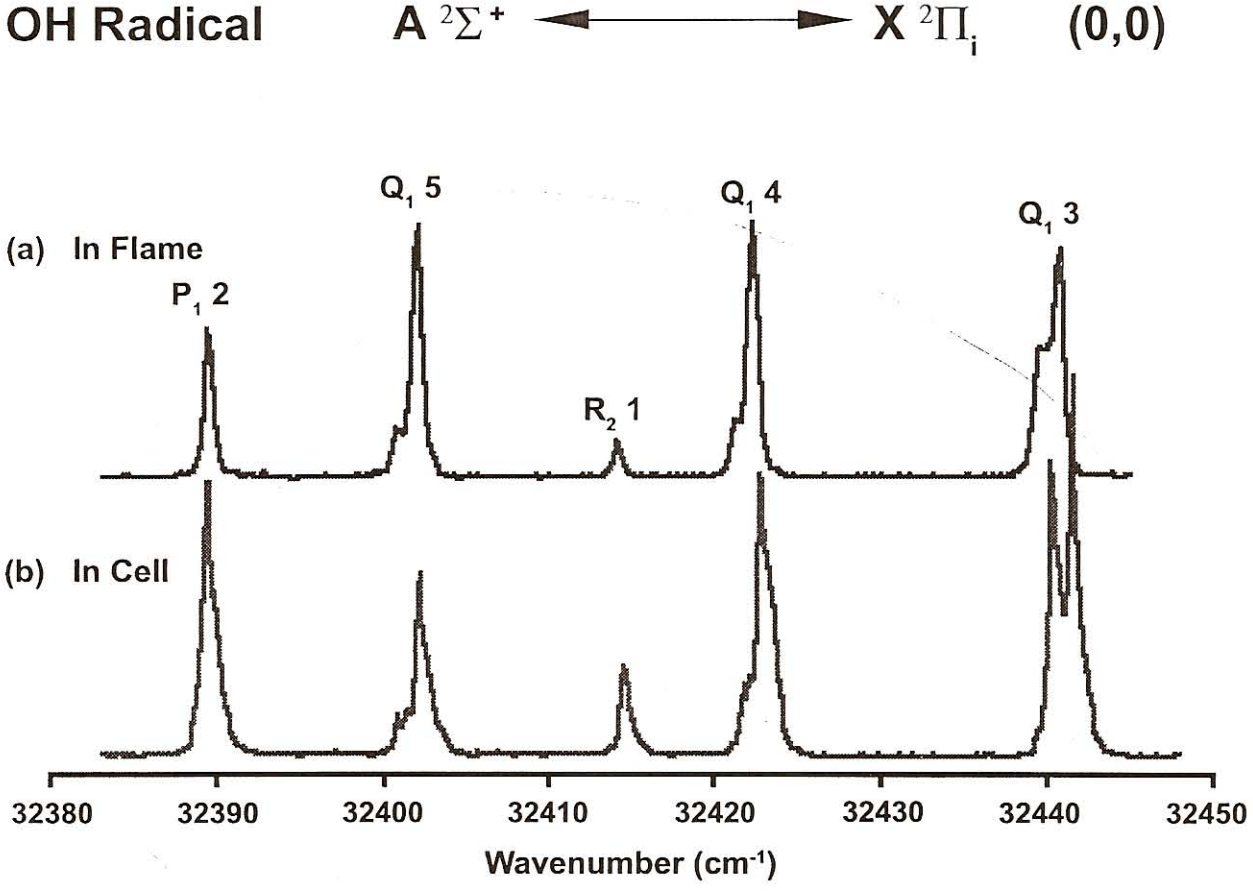

Fig 3. Laser excitation spectrum of the hydroxyl radical (a) in a flame environment and (b) in a cell.

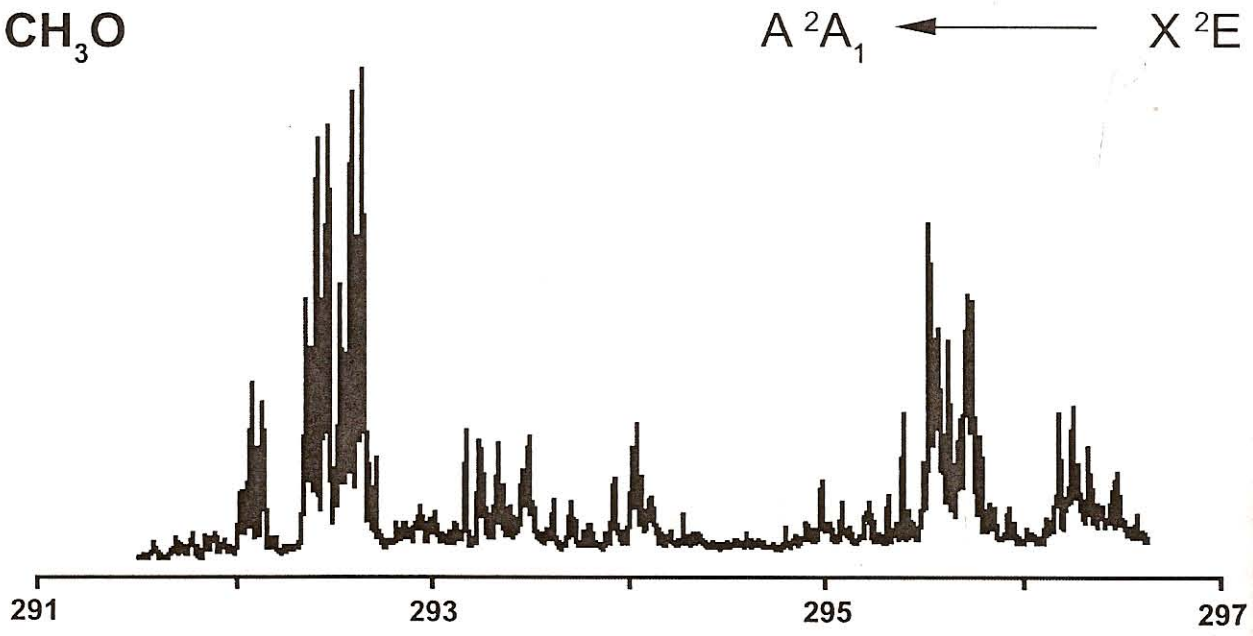

Fig 4. Laser excitation spectrum of the methoxy radical.