Spectroscopy

Rare-Earth Doped All-Solid-State Lasers for Ultraviolet Free Radical Spectroscopy

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Rare-earth doped solid-state lasers are attractive sources of UV light for studying and spectroscopically categorizing free radicals of relevance to combustion and atmospheric phenomena.

The laser-induced fluorescence (LIF) technique in the ultraviolet (UV) region is a noninvasive spectroscopic method of considerable utility in chemical physics investigations. In addition to being suitable for monitoring specific atomic and molecular species and their kinetics (1), it is also important for the visualization and imaging of complex spatial distributions of such species, for example in flame and discharge environments (2). Add to this the very high sensitivity of the LIF approach to spectral data acquisition, and you have an extremely powerful tool for the study of combustion and atmospheric phenomena, because many significant chemical species of atmospheric and environmental importance have strong absorption bands in the UV region. For instance, as noted in the work of Crosley (1), in an atmospheric pressure flame under favorable conditions, the OH radical can be detected spectroscopically around 308 nm at sub-ppb concentration levels and with 1 mm^3-spatial and 10-ns temporal resolution, thereby producing a signal level of ~100 photoelectrons. Besides normal gravity flame combustion, LIF is also an important spectroscopic tool for understanding and elucidation of microgravity combustion phenomena.

The availability of manned laboratory facilities in space offers wonderful opportunities and challenges for in-space science and technology experiments. Over the course of the past three decades, our understanding of stable molecules, ions, and free radicals has been considerably enhanced by the introduction of new and novel experimental techniques, such as infrared laser absorption, microwave absorption, resonantly enhanced multiphoton ionization, optogalvanic spectroscopy, chemiluminescence and LIF spectroscopy. Of these various approaches, chemiluminescence and LIF techniques are particularly suited for the study of molecular species in space. Space-based

spectroscopic studies using sensitive techniques such as LIF should be more informative — compared to other contemporary optical methods of less rigor — and can be used for elucidation of new effects in physics, chemistry, and biology. LIF spectroscopic experiments of significance are based on the use of widely tunable UV lasers. Conventional (commercially available) sources of tunable UV laser radiation are extremely cumbersome and energy-consuming and are not very suitable for in-space/in-flight (or microgravity drop tower) experiments. It was noted at the Second International Microgravity Combustion Workshop (3) that a lack of reliable and portable tunable lasers in the UV region — *"based most probably on solid-state active media"* — was a major constraint in conducting actual microgravity experiments. Indeed, traditional sources of tunable UV laser radiation involve, in addition to a pump laser (usually an Nd:YAG laser with an attached harmonic generator stage), a tunable dye laser in the orange–red region of the spectrum. In turn, the dye laser has to be provided with a dye circulation system and a subsequent stage for frequency-doubling of the dye laser radiation, together with a servo-tuning system (termed the "autotracker") in order to follow the wavelength changes, and also an optical system (called the "frequency separator") for separation of the emanating visible and UV beams. Such a conventional tunable UV laser system is illustrated in Figure 1. It is also worth mentioning that such traditional tunable UV laser systems are not suitable for applications that require fast scanning of UV output wavelengths, owing to the fact that tracking is not feasible beyond certain speeds of spectral sweeping.

In order to overcome many of the shortcomings of tunable UV lasers indicated above, we have developed a tunable solid-state UV laser system based on the interconfigurational 5d-4f transitions

of Ce^{3+} ions incorporated in a single $LiCaAlF_6$ host crystal. Fairly recent developments (4) related to directly pumped all-solid-state tunable UV lasers, based on d-f transitions of Ce^{3+} ions in fluoride crystals and of relevance to direct ultrashort pulse generation, have made rare-earth doped solid-state lasers very attractive sources in the UV range for studying and spectroscopically categorizing transient molecular species of relevance to combustion and atmospheric phenomena. Such free radicals (for example, OH and CH_3O) are important chemical intermediates in the combustion of hydrocarbons both under normal gravity and microgravity conditions.

ALL-SOLID-STATE TUNABLE UV LASER

Based on state-of-the-art developments in quantum electronics, we are going to describe an approach that allows the design of a compact and portable tunable UV laser system that incorporates features necessary for in-space/in-flight spectroscopy experiments. For the purpose of laser excitation, we propose an all-solid-state tunable UV laser that employs *direct* pumping of the solid-state UV-active medium using harmonics from an Nd:YAG laser (which in our case is flashlamp-pumped, but could be [preferably]

diode-pumped). In other words, there would be no need for any frequency transformation *after* the tunability stage, and therefore the so-called "single-knob tuning" of the laser would suffice. Such emerging laser technology will allow users to overcome the earlier cited drawbacks that are characteristic of traditional tunable UV laser systems. Promising results in this direction have been demonstrated for the $LiCAlF_6$: Ce^{3+} (LiCAF:Ce) laser (5–7) and the $LiSrAlF_6$:Ce^{3+} (LiSAF:Ce) laser reported in references 8 and 9. The above-mentioned cerium-doped tunable solid-state technology has the promise to develop into a research area with extensive applications (10).

Figure 2 is a simplified energy level diagram of Ce^{3+} in a $LiCaAlF_6$ crystal showing the 5d-4f lasing transition of LiCAF:Ce that is responsible for the production of UV spectral emission in the wavelength interval of 270–370 nm. We have utilized two optical configurations for the LiCAF:Ce laser: 1) using mirrors to form a nonselective cavity, as shown in Figure 3a, and 2) using a Littrow-mounted diffraction grating to accomplish wavelength tunability, as indicated in Figure 3b. In order to demonstrate the feasibility of the above-cited approach utilizing an all-solid-state platform, we have carried

out preliminary experiments and succeeded in obtaining very promising results studying the LIF spectroscopy of free radicals using a LiCAF:Ce UV tunable laser excitation system.

KEY DESIGN FEATURES

The key factor governing the design of a portable tunable UV laser for LIF excitation of free radicals is a proper "pumping source–active medium" combination that 1) will avoid complications and energy consumption relating to the dye solution circulation and photochemical instability, 2) will use the same efficient laser source for photolysis of suitable precursors (so as to generate the required free radicals) and also for pumping the active medium, and 3) will provide as high as possible "wall-plug" conversion efficiency for the device as a whole. Given a number of state-of-the art possibilities, we chose to adopt the relatively new solid-state tunable UV laser technique based on the $LiCaAlF_6$:Ce^{3+} (LiCAF:Ce) single crystal pumped by the quadrupled output of a commercial Q-switched Nd:YAG laser. Our choice was based on the following considerations:

• The LiCAF:Ce laser is extremely efficient (with reported optical-to-optical conversion efficiency in excess of 47% [11]),
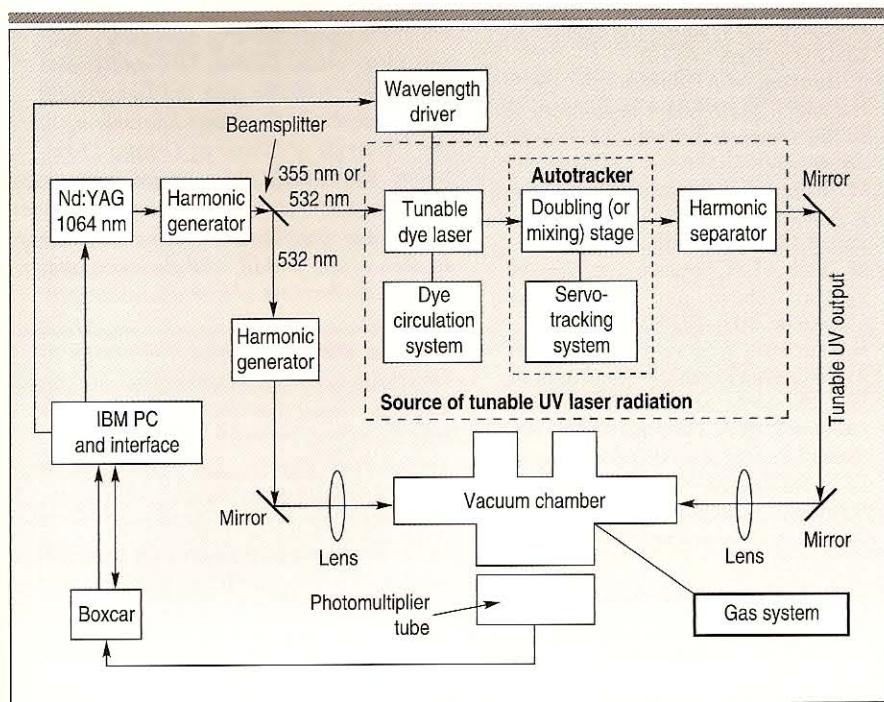
Figure 1. Conventional arrangement for recording the laser induced fluorescence (LIF) excitation spectra of free radicals (following precursor laser fragmentation) using traditional dye laser–based multiple frequency conversion technology for obtaining tunable UV laser radiation.
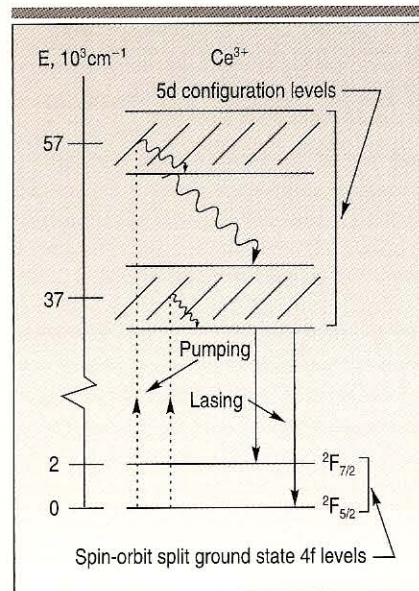
Figure 2. Simplified energy level diagram of the Ce^{3+} ion in a $LiCaAlF_6$ crystal.

and at the same time the active medium is photochemically stable [5–7, 9];

- Its continuous tunability in the UV region (281–315 nm) (12) covers the domain of excitation of the hydroxyl (OH) and methoxy (CH_3O) free radicals,

Figure 3. (a) A simplified schematic representation of the LiCAF:Ce laser using mirrors to form a nonselective cavity; (b) a tunable LiCAF:Ce laser arrangement using a Littrow-mounted diffraction grating.

Figure 4. Experimental arrangement for recording LIF excitation spectra of free radicals (following precursor laser fragmentation) based on a tunable LiCAF:Ce laser with direct UV pumping.

which are important chemical intermediate species in the study of atmospheric and combustion phenomena;

- If necessary, the fourth harmonic of the Nd:YAG laser (at 266 nm) serving as the pumping radiation is efficient enough to also be used for the photodissociation of appropriate precursor species, so as to produce the free radicals (for example, nitrous acid (HONO) yielding OH, and methyl nitrite (CH_3ONO) producing CH_3O) (13);

- The LiCAF:Ce laser is the first known all-solid-state UV tunable device with *direct* pumping by a Q-switched, frequency-quadrupled, diode-pumped Nd:YAG laser which would allow the design and development of a compact and portable laser spectroscopic unit that would prove useful for in-flight measurements.
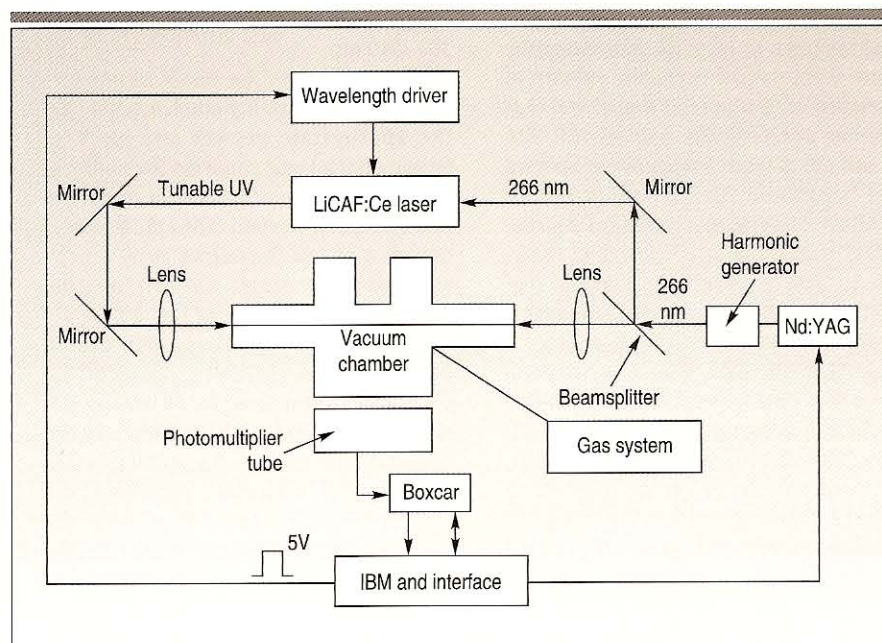
Combustion-associated free radicals, such as hydroxyl (OH) (14) and methoxy (CH_3O) (15) have been the subject of extensive experimental investigations (and are also well-described theoretically and therefore considered to be good molecular model subjects). These radicals have analytically convenient excitation bands located in the 280–298-nm spectral region. For our initial experiments (15), we chose the methoxy radical, because its LIF is relatively weak, and thus, observation of its LIF signal using an all-solid-state tunable laser would be good proof of feasibility of the use of rare-earth doped solid-state lasers for LIF spectroscopy of free radicals, as compared with, say, observation of strong OH fluorescence.

EXPERIMENTAL ARRANGEMENT AND ITS CHARACTERISTICS

The experimental arrangement used for recording the excitation spectra of free radicals in the near UV spectral region is based on the LiCAF:Ce tunable laser (and is shown in Figure 4). The 266-nm YAG output was split into two beams of equal intensity, one of which was used for photolyzing the free radical precursor and the other was used to pump the laser crystal. Three important characteristics of the computer-controlled device were: 1) the pulse repetition rate of the system was 10 Hz; 2) the LiCAF:Ce tunable laser output had a spectral bandwidth of $0.15\ cm^{-1}$; and 3) the speed of spectral scanning was 0.5 nm/min. Tunability of the LiCAF:Ce laser was provided by a step-motor-driven diffraction grating. We employed an optical scheme with coun-

terpropagating photolysis and excitation beams focused by fused silica lenses into a reaction vacuum chamber (as shown in Figure 4).
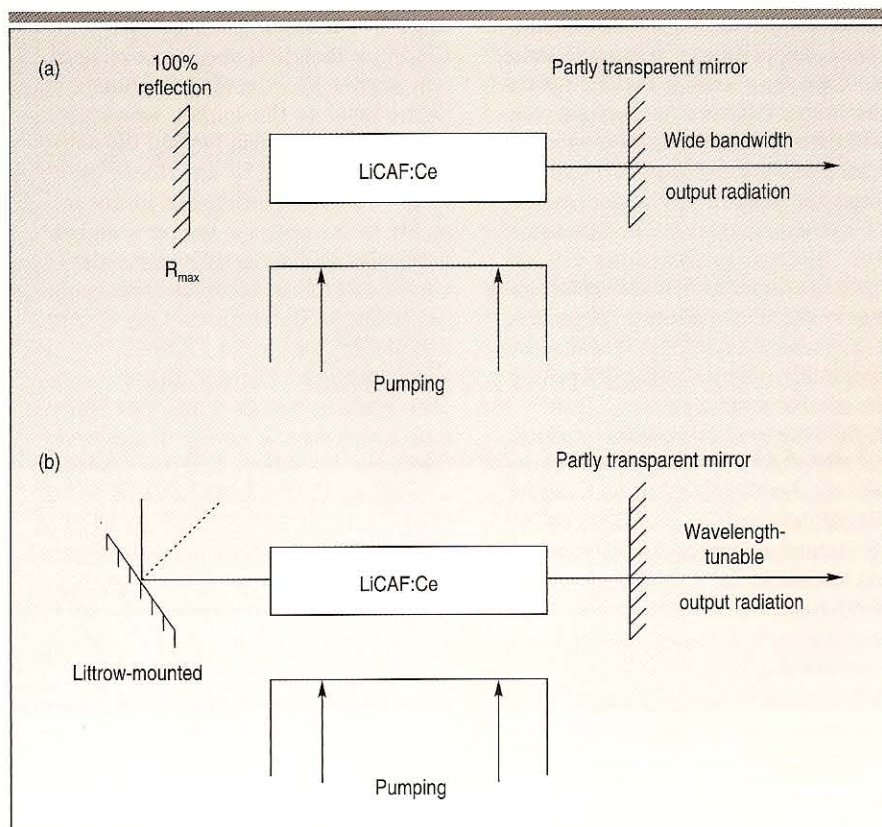
LIF SPECTRUM OF THE METHOXY RADICAL

Figure 5 represents a typical excitation spectrum of the methoxy (CH_3O) radical in the spectral region 291.5–296.5 nm obtained using the above-cited arrangement by photodissociating the CH_3ONO precursor. Our preliminary laboratory experiments thus show that the idea of using the LiCAF:Ce laser as an excitation source, in conjunction with a 266-nm pump laser that is also used for photolysis of the precursor species, provides a viable option for routine analytical investigations of combustion processes in space under both normal gravity and microgravity conditions.

LIF SPECTRUM OF THE HYDROXYL RADICAL

As indicated earlier, the LIF signal from
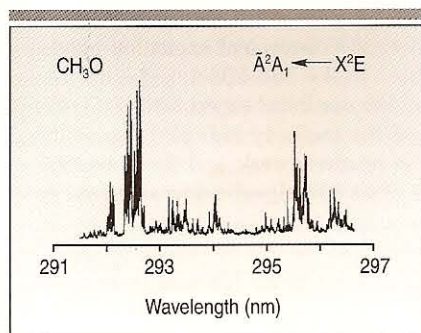
Figure 5. LIF excitation spectrum of the methoxy free radical in the 291–297-nm region recorded with the LiCAF:Ce solid-state laser system.
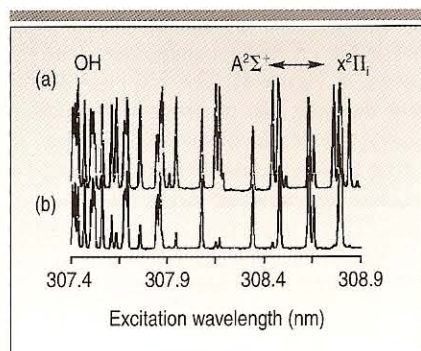
Figure 6. LIF excitation spectra of a propane–air flame showing the hydroxyl radical signature spectrum in the 307.4–308.9-nm region recorded with a registration wavelength of (a) 324 nm and (b) 330 nm.

OH radicals is quite strong and distinctive (compared to other radicals born in flames), and usually they may be detected with few complications. As a result, the requirements for the tunable UV laser output energy are not so stringent. Thus, by choosing the OH radical as the primary species for in-space combustion studies, the weight–dimension characteristics of the analytical unit (including the tunable UV laser and the PMT-detection system) can be minimized. Such considerations are extremely important for airborne measurements in flight and aboard spacecraft, and they also provided the incentive for studying OH radicals in the framework of the present project.

In the course of our studies, we have found that the LIF excitation spectra of alkane-air flames (that can be used for studying combustion processes under both normal and microgravity conditions) excited in the region of the $A\,^2\Sigma^+ - X\,^2\Pi$ (0,0) OH-absorption bands are very sensitive to changes in experimental conditions (the spectra are both temperature-sensitive and positionally sensitive in flames). Especially noticeable and valuable for analytical spectroscopic measurements is the sensitivity to a particular wavelength of registration. We define the registration wavelength as the wavelength setting of the monochromator used to disperse the laser-induced fluorescence associated with the free radical being investigated (which, in this case, happens to be OH). For example, Figure 6 shows LIF excitation spectra of a propane–air flame recorded at two registration wavelengths, namely, (a) 324 nm and (b) 330 nm, respectively. Spectra were obtained using our tunable LiCAF:Ce laser as an excitation source, similar to the approach given in reference 16. The bandwidth for spectral registration was fwhm = 4 nm (measurement was accomplished using a monochromator, which for in-space measurements can be replaced by a lightweight and compact interference filter). A comparison of Figures 6a and 6b indicates a drastic change in the appearance of the excitation spectra with a change in registration wavelength of only 6 nm. The reasons for such behavior are still under consideration, but it is quite clear already that such pronounced alkane–air flame features may be extremely useful for combustion studies under microgravity conditions.

PORTABLE SPECTROSCOPIC UNIT BASED ON THE LiCAF:Ce LASER

The proposed analytical spectroscopic unit could also be used for excitation of other free radicals (such as C_2H_5O and CH_3S) as analytical species in combustion studies by extending the tunability of the laser to the longer wavelength side of the UV region beyond the aforementioned 280–315-nm range. Such long-wavelength extension in the tunability in the near-UV region would enhance the application potential of the LiCAF:Ce tunable laser considerably. According to our data (17), incorporation of Ce^{3+} ions in the $LiCaAlF_6$ host in a Bridgman-Stockbarger growth procedure leads to so-called multisite activation, which means that Ce^{3+} ions enter the lattice by substituting Ca^{2+} ions in several structure-nonequivalent positions. Three types of structure-nonequivalent Ce^{3+} centers have been discovered by now, and it has been shown that the real LiCAF:Ce fluorescence spectrum is a superposition of the "partial" spectra arising from different Ce^{3+} optical centers (18). The latter effect makes the real fluorescence spectrum significantly wider than the spectrum from individual "partial" Ce^{3+} centers (18). The relative contents of centers of different types in a LiCAF:Ce crystal can be controlled by changing the growth conditions, which in turn holds promise for devising a LiCAF:Ce laser that has the ability to cover completely the spectral region of 280–340 nm.

Figure 7 shows the result of our preliminary UV tunability studies (following the appropriate growth and spectroscopic efforts) and confirms the ability of the LiCAF:Ce laser to lase in the wavelength region beyond 320 nm. Figure 7 depicts a plot of the output pulse energy vs. tunable wavelength showing the long-wavelength tunability of the LiCAF:Ce laser based on the Bridgman-Stockbarger grown multisite activated LiCAF:Ce crystal sample. With the obtained long-wavelength tunability in the 321–329-nm region, we succeeded in recording LIF excitation spectrum of the ethoxy (C_2H_5O) free radical over the range of 323.8–328.5 nm employing LiCAF:Ce laser excitation. The LIF excitation spectrum of C_2H_5O is indicated in Figure 8 and illustrates the anticipated application potential for the LiCAF:Ce laser with the extended long-wavelength tunability.
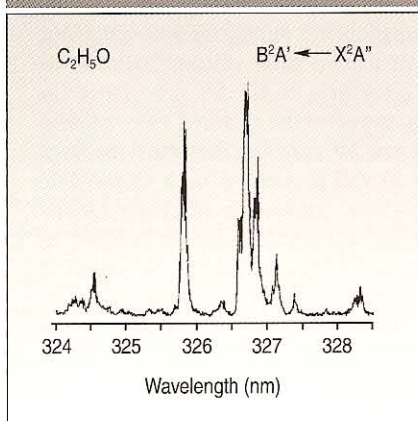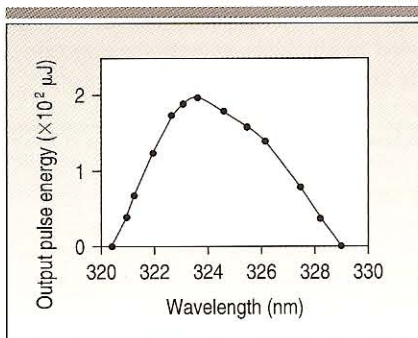
Figure 7 (top). A plot of the output pulse energy vs. tunable wavelength showing the long-wavelength tunability of the LiCAF:Ce laser based on the Bridgman-Stockbarger grown multisite activated LiCAF:Ce crystal sample.

Figure 8 (bottom). Laser excitation spectrum of the ethoxy free radical in the 323.8–328.5-nm region recorded with the LiCAF:Ce all-solid-state laser.

CONCLUSIONS

Our investigations have exhibited significant promise for the use of rare-earth doped crystals in the development of an all-solid-state laser spectroscopic unit that will provide tunable radiation in the 280–330-nm spectral region for airborne microgravity measurements, and thereby help in the elucidation of ultraviolet free radical spectroscopy as it relates to atmospheric and combustion phenomena.

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