Combustion Diagnostics Using a Difference-Frequency-Generation Laser Tunable from 12.6 to 15 μm

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Abstract: We developed a new diagnostic technique based on a widely tunable difference-frequency-generation laser for combustion studies. We applied this technique to probe benzene near 14.84 μm during its formation from propargyl radicals.

1. Introduction

Optical diagnostics have played a central role in modern studies of combustion and chemical kinetics research. In particular, laser absorption spectroscopy (LAS) has been of high interest since it provides non-intrusive, quantitative, high spatial and temporal resolution, and species-specific measurements of temperature, pressure, and composition of chemical species. Furthermore, combining LAS with shock tubes has provided a unique tool to understand and develop chemical kinetics of combustion reactions at high temperatures and pressures. The selection of applied wavelength(s) to probe the species of interest is(are) critical to achieve high measurement sensitivity and selectivity. Many gaseous chemical species of interest in combustion research, e.g., CO, CO₂, NO_x, and hydrocarbons, do not have easily accessible electronic transitions, but they show strong fundamental ro-vibrational absorption bands in the mid-infrared (MIR) spectral range. Light absorption by these MIR bands can be used for high-sensitivity sensing of such species. This is one of the major motivations to develop new MIR laser sources that can be exploited in optical diagnostics for combustion and chemical kinetic studies. Among MIR laser sources, nonlinear frequency conversion based lasers have several unique merits, such as a broad tunability across the desired wavelength range. In our present work, we have developed and applied a tunable difference-frequency-generation (DFG) laser system emitting between 12.6 and 15 μm to design a new diagnostic technique for interference-free and sensitive measurements of gaseous species in combustion environments. This diagnostic technique has been demonstrated in a high-temperature experiment of benzene formation from propargyl radicals.

2. Diagnostic technique

Fig. 1. Schematic of (a) the DFG laser setup and (b) the cross-section of the shock tube. EC-QCL: external-cavity quantum cascade laser; OI: optical isolator; CM: concave mirror; BC: beam combiner; PM: parabolic mirror; M: mirror (flat); OP-GaAs: orientation-patterned GaAs crystal; LF: long-pass filter; BS: beam splitter; D: detector.

Figure 1(a) shows a schematic of the laser system designed to emit between 12.6 and 15 μm as a result of the DFG process between an external-cavity quantum-cascade-laser (EC-QCL) and a CO₂ gas laser in a nonlinear, orientation-patterned GaAs crystal. The EC-QCL is tunable between 5.49 and 5.71 μm and was used as a pump source, while the CO₂ gas laser provided the signal beam tunable between 9.23 and 10.86 μm . Further details about the presented DFG laser can be found in [1]. A long-pass filter (LF) was used to filter out both the pump and signal wavelengths. The DFG laser beam was split using a beam splitter in two beams, as shown in Fig. 1(b). The reflected beam was directly focused onto an HgCdTe detector (D₁) using a parabolic mirror (PM₃), while the primary beam was aligned through the shock-tube cross-section and then focused onto another similar detector (D₂) using PM₄. We installed an LF in front of each detector to reduce optical noise and to minimize the thermal radiation from the hot gases in the shock tube. We performed measurements in a stainless steel, low-pressure shock-tube (LPST) facility.

This LPST has an inner diameter of 14.22 cm and is separated into two sections, driver and driven, separated by a thin polycarbonate diaphragm. Shock waves are generated by pressure-bursting of the diaphragm with a high-pressure gas (helium) in the driver section, while the test gas mixture is contained in the driven section. Laser measurements were made at a distance of 2 cm from the end wall of the driven section. Further details about the shock tube can be found in [2].

3. Benzene measurements

Fig. 2. (a) Absorption cross-section of benzene vs. temperature. The blue dashed line in (a) is the best fitting using a bi-exponential function (inset). (b) Time-resolved benzene-mole fraction. The right-side y-axis in (b) shows the pressure trace.

Benzene (C_6H_6) is the simplest aromatic hydrocarbon and is a primary intermediate formed during the fuel-rich combustion. The chemistry of benzene at high temperatures has an important role in polycyclic aromatic hydrocarbons (PAH) and soot formation. The strongest vibrational feature of benzene in the MIR range is the Q-branch of the ν_{11} vibrational band. Hence, for benzene measurements, the DFG laser was tuned to $14.838 \mu m$ which is the peak of the Q-branch. We applied direct LAS to measure the absorption cross section (σ) of benzene. Measured absorbance (A) is related to the physical parameters of the species (benzene) and experimental conditions via the Beer-Lambert relation, $\sigma = A \cdot T \cdot k_B / x \cdot P \cdot L$, where T , P and x are the temperature, pressure, and the benzene mole fraction, k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23} J/K$) and L is the absorption path length ($L = 14.22 cm$). Figure 2(a) shows the temperature dependence of the measured absorption cross-sections of benzene over the temperature range of 553 – 1473 K. The pressure varied between 1.17 and 2.48 bar in these experiments. The blue dashed line in Fig. 2(a) show the best fitting to the experimental data points using a bi-exponential function.

Ultimately, we applied the diagnostic technique to monitor benzene formation from propargyl radicals. A mixture of 4.6% propargyl iodide (C_3H_3I) in argon was shock-heated to reach reflected shock temperature and pressure of 961 K and 1.36 bar, respectively. The measured time-resolved mole-fraction of benzene is shown in Fig. 2(b) as a solid red line and compared with the simulation (dashed blue line) using a benzene chemical model [3,4]. For this particular case, the model predictions agreed very well with our measurements. However, as the PAH and benzene chemistry is not yet fully resolved in literature, this diagnostic will prove to be highly useful for investigating the details of PAH chemistry.

4. Summary

We have reported the development of a new diagnostic technique based on a DFG laser emitting between $12.65 - 15 \mu m$ as a result of the DFG process between an EC-QCL and a CO_2 gas laser in an OP-GaAs crystal. We have applied this technique to probe benzene at $14.838 \mu m$ in a shock tube. The absorption cross-section of benzene was measured at high temperatures between 553 and 1473 K. Furthermore, we temporally monitored and quantified the benzene formation from propargyl iodide (C_3H_3I). The diagnostic can be used to probe C-H bending vibrational modes of many other species.

References

- [1] M. K. Shakfa *et al.*, “A $12.6 - 15 \mu m$ Mid-IR Source Based on Difference Frequency Generation in Orientation-Patterned GaAs,” in *2019 Conference on Lasers and Electro-Optics Europe and European Quantum Electronics Conference*, OSA Technical Digest (Optical Society of America, 2019), paper cd_11_3.
- [2] S. Mani Sarathy *et al.*, “A comprehensive combustion chemistry study of 2,5-dimethylhexane,” *Combust. Flame* **161**, 1444–1459 (2014).
- [3] J.A. Miller and S.J. Klippenstein, “The Recombination of Propargyl Radicals and Other Reactions on a C_6H_6 Potential,” *J. Phys. Chem. A* **107** (39) 7783–7799 (2003).
- [4] R.S. Tranter *et al.*, “Dissociation of C_3H_3I and rates for C_3H_3 combination at high temperatures,” *Proc. Combust. Inst.* **33** (1) 259–265 (2011).