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**Mid-infrared pumped laser-induced thermal grating spectroscopy for detection of acetylene
in the visible spectral range**

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Abstract

We present mid-infrared laser-induced thermal grating spectroscopy (IR-LITGS) using excitation radiation around 3 μm generated by a simple broadband optical parametric oscillator (OPO). Acetylene as a typical small hydrocarbon molecule is used as an example target species. A mid-infrared broadband OPO pumped by the fundamental output of a Nd:YAG laser was used to generate the pump beams, with pulse energies of 6-10 mJ depending on the wavelength. The line width of the OPO idler beam was $\sim 5\text{ cm}^{-1}$, which is large enough to cover up to six adjacent acetylene lines. The probe beam was the radiation of a 532 nm cw solid state laser with 190 mW output power. Signals were generated in atmospheric pressure gas flows of N_2 , air, CO_2 and Ar with small admixtures of C_2H_2 . A detection limit of less than 300 ppm was found for a point measurement of C_2H_2 diluted in N_2 . As expected, the oscillation frequency of the IR-LITGS signal was found to have a large dependency on the buffer gas, which allows determination of the speed of sound. Moreover, the results reveal a very strong collisional energy exchange between C_2H_2 and CO_2 compared to the other gases. This manifests as significant local heating. In summary, the IR-LITGS technique enables spectroscopy of fundamental vibrational transitions in the infrared via detection in the visible spectral range.

Keywords: hydrocarbon detection, laser-induced gratings, LITGS, nonlinear optical spectroscopy, acetylene, quenching

Introduction

Laser-induced thermal grating spectroscopy (LITGS) is a nonlinear optical method, which allows the analysis of gases, liquids and solids. In a LITGS experiment, two pulsed laser beams (often referred to as pump beams) are overlapped coherently to create an interference pattern in the intersection region. When the laser frequency is tuned to a transition of a target species, the molecules absorb photons and thermalization takes place subsequently. Since the intensity in the intersection region is spatially modulated, regions of high intensity will end up with higher temperature than low intensity regions. This leads to a transient density modulation, and thus, a laser-induced spatially-periodic modulation of the refractive index, i.e. a laser-induced grating (LIG). For completeness, we note that electrostriction is also taking place, but it can usually be neglected in case of strong absorption. A third continuous-wave laser beam (often referred to as probe beam), is aligned to cross the LIG at the Bragg angle. The power of the diffracted probe laser radiation represents the signal. Its detection with high temporal resolution reflects the temporal evolution of the LIG and carries information about the local composition and thermophysical properties of the medium.

Originally, signals from LIGs were observed as an undesirable interference to degenerate four-wave mixing (DFWM) signals, especially at higher pressures.^{1,2} However, LITGS has been developed from an interfering signal into a versatile laser technique, which can offer accurate measurements of multiple parameters including species concentration, temperature, speed of sound and viscosity of a gas.³ Consequently, numerous applications were reported over the past two decades. For example, LITGS has been successfully employed to detect OH in the post-flame region of a H₂/O₂ flat flame.⁴ A great advantage of LITGS over other resonant four-wave mixing techniques is an increase in the signal intensity at higher pressures.⁵ Hemmerling et al. have

employed LITGS to detect H₂O in the second overtone OH stretch around 817 nm using a near infrared OPO laser.⁶ Roshani et al.⁷ employed LITGS to determine simultaneous fuel/air ratio and gas temperature in a direct injected spray. Williams et al.⁸ used LITGS to study the quenching effects of oxygen on toluene. Kozlov et al. used LIGS to study highly excited overtone and combination vibrational states of CH₄,^{9,10} and simultaneous measurement of flow velocity and temperature.¹¹ Latzel and Dreier have demonstrated sound velocity and heat conduction measurements using near-infrared laser radiation at 1064 nm and 1890 nm.¹² In the long-wavelength infrared spectral region, LITGS measurements using CO₂ lasers as pump lasers have been used for detection of C₂H₄,¹³⁻¹⁵ CH₃OH,¹³ NH₃.¹⁵ Thermal LIGs effects have also been observed in degenerate four-wave mixing experiments of C₂H₄ and SF₆ performed with CO₂ lasers.¹⁶

Mid-infrared laser spectroscopy offers an opportunity to probe molecules that have no easily accessible transitions in the visible and UV region. Prominent examples include CH₄, C₂H₂, HCN, HF and HCl. Coherent laser techniques like degenerate four-wave mixing (DFWM) and polarization spectroscopy (PS) offer an advantage over incoherent techniques in the mid-IR region because of the ability to efficiently discriminate against background mid-IR radiation, which is always present, especially in hot combustion environments. Traditionally, coherent non-linear mid-IR spectroscopy was held back by the relatively low availability of suitable laser sources and sensitive detectors in this spectral region. Only in recent years, the development of nonlinear frequency mixing crystals have made it possible to generate pulsed laser beams with relatively high laser energy. However, even the best available detectors in the mid-IR region, such as cryogenic InSb photodetectors, have less sensitivity and higher noise levels compared to detectors in the visible and near-infrared region. One approach to overcome this problem has recently been

proposed by Dam et al.¹⁷ They developed a new mid-IR detector that uses upconversion of light to transform the mid-IR signals to near-infrared wavelengths, where much more efficient and low-noise detectors exist. IR-DFWM signals have been successfully detected with this upconversion detector, resulting in significantly improved detection limits.¹⁸

An alternative approach would be to generate the signal itself in the visible or near-infrared range. The LITGS technique offers this opportunity as the pump laser can be tuned to the molecular transitions in the mid-IR while the probe laser wavelength can, in principle, be chosen arbitrarily. In other words, IR-LITGS has the possibility for sensitive species-selective detection of molecules in the mid-infrared spectral region with signal detection using the sensitive, low-noise detectors widely available for visible wavelengths. Moreover, a pulsed four-wave mixing technique, IR-LITGS provides high spatial and temporal resolution. Its beneficial pressure dependence opens up the application of mid-IR laser techniques in high-pressure environments.

In this paper, we demonstrate, for the first time to our knowledge, the generation and detection of mid-infrared laser-induced thermal gratings (IR-LITGS) in the gas phase using pump laser wavelengths around 3 μm . Signals were obtained utilizing absorption of acetylene molecules. For this purpose, IR-LITGS was applied to atmospheric pressure gas flows of N_2 , Ar, air or CO_2 with small admixtures of C_2H_2 . The pulsed mid-IR pump laser radiation at $\sim 3 \mu\text{m}$ is generated by a compact optical parametric oscillator (OPO) pumped by the fundamental 1064 nm laser beam from a Nd:YAG laser.

Theory

The theory of LIGs has been presented several times before (see e.g. ^{3,19-22}) and the technique was recently reviewed by Kiefer and Ewart.⁵ LIGs are usually generated in a geometry similar to the forward phase matching geometry of DFWM. Two laser beams with wavelength λ_{pump} are crossed at an angle θ , generating an interference fringe pattern with a characteristic grating spacing Λ according to³

$$\Lambda = \frac{\lambda_{pump}}{2 \sin\left(\frac{\theta}{2}\right)} \quad (1)$$

If the laser is resonant with a transition of a species in the intersection region, the molecules will be excited along the fringes of high laser intensity. Due to molecular collisions, the excited molecules' internal energy will be transformed into thermal energy, creating a thermal LIG (LITG) with alternately high and low temperature across the fringes of the interference pattern. This LITG then decays exponentially depending on the thermal diffusivity of the medium, e.g. a gas or a liquid.

When the LITG is formed, the fast changes in temperature will rapidly create a density modulation, which eventually results in two acoustic waves propagating perpendicular to the fringe plane in opposite direction; consequently the formation of a standing wave. This wave, added to the stationary density modulation from the LITG, will cause a modulation of the refractive index that oscillates in time at the frequency f_{osc} given by Λ and the speed of sound v_s as³

$$f_{osc} = \frac{v_s}{\Lambda} \quad (2)$$

The acoustic waves will decay exponentially due to viscous damping effects. In addition, as time progresses, the waves will travel across the intersection volume of the two lasers in a direction perpendicular to the interference plane. If the size of the crossing region is small enough, the acoustic waves will travel out of the crossing region during the lifetime of the LITG. Thus, the oscillations in the LITG will also decay exponentially according to the acoustic transit time τ_{tr} ²¹

$$\text{decay} \propto \exp(-2t^2/\tau_{tr}^2), \quad \tau_{tr} = \frac{w}{\sqrt{2}v_s \cos\left(\frac{\theta}{2}\right)} \approx \frac{w}{\sqrt{2}v_s} \quad (3)$$

where w is the beam radius at the crossing point.

The dynamics of the LIG can be studied by sending in a probe laser incident on the grating at the Bragg angle θ_B , given by

$$\sin(\theta_B) = \frac{\lambda_{\text{probe}}}{2 \cdot \Lambda} \quad (4)$$

where λ_{probe} is the wavelength of the probe laser. Note, that equation 4 is valid for first-order diffraction. The probe laser is usually a cw laser and its wavelength can be chosen arbitrarily. The signal is formed by the probe laser scattering off the LITG. The signal intensity scales linearly with the probe laser power and quadratically with the concentration of the absorbing species.¹⁹ The stationary temperature grating generates a fast rising signal, which then decays exponentially. The contribution of the acoustic wave is shown as an oscillation in the signal intensity superimposed on the signal from the stationary part of the LITG. The contrast of the oscillations is a measure of the relative strength of the stationary and acoustic parts of the LITG, and is defined as⁸

$$\text{contrast} = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}} \quad (5)$$

where $I_{\max}$ is the signal intensity at the peak of the oscillation and $I_{\min}$ is the signal intensity at the following minimum. For a contrast = 1, the acoustic and temperature gratings signal amplitude are of equal intensity, corresponding to instantaneous and complete relaxation of the molecular internal energy.⁸ If the energy deposition into the medium is slower, the acoustic part of the LITG is reduced with respect to the stationary LITG. If the energy deposition time is longer than the time that it takes for the acoustic wave to travel across one grating period Λ , the acoustic wave amplitude (and the corresponding contribution to a LITG) will be reduced.

Experiment

A schematic of the experimental setup is shown in Figure 1. The pump laser used for the IR-LITGS experiments is the idler beam from an infrared OPO (GWU, versaScan-L 1064) pumped by the 1064 nm fundamental beam from a Nd:YAG laser (Spectra Physics, PRO 290-10) with ~310 mJ pulse energy and 8-10 ns pulse duration. The OPO wavelength can be tuned from 3100 to 3350 cm^{-1} with 6-10 mJ output energy and ~5 ns pulse duration. The probe beam was the radiation of a cw solid state laser with wavelength 532 nm and output power 190 mW (Laserglow Technologies, LRS-0532-PFM-00300-01).

In order to ease the alignment of the mid-IR beams, the OPO laser beam was spatially overlapped with the beam from a HeNe-laser. A specially coated CaF_2 plate²³ was used to split the mid-IR beam into two parallel pump beams of equal intensity separated by 12.7 mm. A specially designed 5.2 cm long sapphire rod was placed in the path of one of the beams to compensate for the

difference in path length between the two pump beams. This is crucial because of the bandwidth of the OPO radiation, which was $\sim 5 \text{ cm}^{-1}$ FWHM, corresponding to a coherence length of $\sim 1 \text{ mm}$. It has been demonstrated by Kozlov et al. that using broadband pump lasers requires a careful alignment in order to ensure coherent superposition of the beams.²⁴ Stampanoni-Panariello et al.²¹ have also shown the dependence of the coherence length and the beam path difference on the signal, and found that the alignment is especially crucial for broadband lasers. The non-Gaussian shape of the pump beams and different divergence in horizontal and vertical direction presented another challenge in the alignment.

The pump beams were focused by a 2-inch CaF_2 lens with 300 mm focal length, giving a crossing angle of 2.4° and hence a grating spacing of $72.8 \text{ }\mu\text{m}$. The phase-matching was obtained in a planar BOXCARS geometry. For this purpose, the probe beam was aligned to cross the LIG at an angle of 0.21° , which is the Bragg angle for this grating spacing and the probe laser wavelength 532 nm. This meant the signal beam was reflected at an angle 0.42° with respect to the probe beam. The excitation volume, defined by the overlap of the crossing pump lasers, had a dimension of $65 \times 2 \times 0.5 \text{ mm}^3$. After the interaction region, an aperture was used to separate the probe and signal beams and the signal was directed to a photomultiplier tube (PMT). The PMT was placed far enough away from the measurement that the probe and signal beams were not overlapped at the PMT. A 532-nm bandpass filter was used to minimize interference. The PMT was connected to a digital oscilloscope, where the signal was recorded. In order to compensate for shot-to-shot variations in the mode structure of the OPO beam, 500 pulses were averaged for each measurement condition.

The gas flow was supplied through a McKenna type porous plug burner in order to ensure a homogeneous mixture in the measurement volume. C_2H_2 was mixed with a buffer gas flow of N_2 ,

Ar, air, or CO₂. The concentration of C₂H₂ in the buffer gas was controlled by regulating the relative flows using mass flow controllers.

Figure 1: Schematics of the experimental setup. *M*: aluminum mirror, *DM*: dichroic mirror, *L*: CaF₂ lens, *A*: aperture, *IF*: interference filter 532 nm, *PMT*: photomultiplier tube, *BP*: BOXCAR plate beam splitter, *S*: sapphire rod.

Results and discussion

LITGS generation and signal characteristics

One set of IR-LITGS measurements was carried out with the OPO tuned to a center wavenumber of 3256 cm⁻¹. The spectral profile of the broadband IR-OPO was measured by dispersing a small part of the IR laser beam with a grating (600 grooves/mm, blazed at 2.5 μm) into an IR CCD camera (Santa Barbara Focal Plane, SBF LP134). Figure 2 shows the spectral profile of the OPO infrared output, averaged over 500 laser shots, together with the absorption spectrum of acetylene. The OPO spectrum clearly reveals the mode structure covering the range from 3252 to 3262 cm⁻¹. The profile is slightly asymmetric and exhibits a FWHM of ~5 cm⁻¹. The OPO output overlaps with a number

of P -branch absorption lines of acetylene corresponding to the 0010^00^0 - 0000^00^0 and the $010(11)^0$ - 0000^00^0 vibration bands.

Figure 2: The spectral profile of the OPO laser centered at 3256 cm^{-1} , averaged over 500 laser pulses (blue), and the absorption coefficient of C_2H_2 (green) for a concentration of 4500 ppm in nitrogen and of pure CO_2 (red), at 296 K and 1 atm. The data for the spectroscopic simulations were taken from the HITRAN database.²⁵

Figure 3: A simulation of the absorption coefficient between 3224 and 3234 cm^{-1} of C_2H_2 (blue), for a mole fraction of 4500 ppm in nitrogen, and of pure CO_2 (red), at 296 K and 1 atm. The data for the spectroscopic simulations were taken from the HITRAN database.²⁵

Another series of IR-LITGS experiments was performed with the OPO tuned to 3229 cm^{-1} as the center wavenumber. Figure 3 shows the simulated absorption spectrum for C_2H_2 and CO_2 in the relevant interval used for the measurements. While CO_2 has absorption lines in both wavelength intervals plotted in Figs. 2 and 3, the absorption cross section is very weak in both ranges (~ 4 orders of magnitude weaker than the C_2H_2 lines, even comparing pure CO_2 with highly diluted C_2H_2 , i.e. a concentration of 4500 ppm in an arbitrary buffer gas). These spectra indicate that the CO_2 absorption effects on the IR-LITGS signal from C_2H_2 diluted in CO_2 can be neglected.

As an example, the IR-LITGS signal generated in 4169 ppm C_2H_2 diluted in N_2 at OPO wavelength 3229 cm^{-1} is shown in Figure 4. The red curve shows the temporal profile of the Nd:YAG pump beam, detected with a photodiode, and the blue curve shows the IR-LITGS signal. Note that the IR pump beams from the OPO will arrive at the measurement volume delayed with respect to the plotted Nd:YAG pulse. However, this delay is small (in the order of 10 ns) compared to the timescale of microseconds in the figure. Hence, the Nd:YAG pulse gives a good impression of the sequence and timing of the signal generation and detection, illustrating the timescale of the collisional thermalization process in the gas. There is no noticeable contribution from a non-resonant electrostrictive LIG in the signal.

Initially, the signal rises and reaches its maximum after four oscillation periods. The behavior at the rising wing is determined by the grating spacing and the quenching time.⁸ The amplitude of the oscillations in the signal is damped with time and disappear after $\sim 6\text{ }\mu\text{s}$, which is approximately the time it takes for an acoustic wave in N_2 to leave a probe volume exhibiting a width of 2 mm in the direction of the sound propagation. Thus, the acoustic transit time is responsible for the damping of the oscillations. A second possible mechanism is sound attenuation by viscous

damping, which can be characterized using the Stokes law of sound attenuation. The exponential constant α is given by

$$\alpha = \frac{2 \cdot \eta \cdot f^2}{3 \cdot \rho \cdot v_s^3} \quad (6)$$

where η is the dynamic viscosity, f is the sound frequency, ρ is the density and v_s is the speed of sound. For nitrogen under the given conditions and using the frequency determined from the IR-LITGS signal, the exponential constant is in the order of 5 m^{-1} (see Electronic Supplementary Document for details). Hence, sound attenuation effects through viscous damping can be neglected on the length scale of the measurement volume in our experiment. The thermal diffusivity can also have an effect on the damping of the acoustic waves, but this too is negligible in our measurements.

It can be noted that the oscillations disappear after $\sim 4 \text{ } \mu\text{s}$ and appear again at $\sim 4.5 \text{ } \mu\text{s}$. This phenomenon can have two origins: (1) the presence of distinct regions within the probe volume with different temperatures and/or different chemical composition, and (2) a geometrical effect in terms of the generation of two slightly different grating structures. The first reason can be ruled out as the gas in the probe volume was supplied through the porous metal plug of the McKenna burner, which ensured a homogeneous temperature and composition distribution. The second reason is most likely because of the mode structure and spatial profile of the broadband OPO radiation. The focal spot of the IR radiation is relatively large. Hence, if different gratings are formed at different locations in the intersection region, the acoustic waves can reach the probed volume at different times. This leads to the observed “beat” in the oscillations.

The IR-LITGS signal in Figure 4 reaches its peak at $\sim 1 \mu\text{s}$, and the exponential decay time τ_d of the stationary part of the LITG (found by fitting a $A \cdot e^{-t/\tau_d}$ curve to the decaying part of the signal) is $3.4 \mu\text{s}$. The contrast of the oscillations in Figure 4 is ~ 0.23 . This indicates that the thermalized energy exchange in the medium is relatively slow compared to the inter-fringe transit time of the acoustic wave, resulting in the stationary part of the LITG dominating over the acoustic part.⁸

Figure 4: IR-LITGS signal (blue) generated in 4169 ppm C_2H_2 diluted in N_2 with the OPO wavelength centered at 3229 cm^{-1} and the temporal profile of the Nd:YAG pump laser beam (red).

Concentration dependence

In order to use IR-LITGS as a tool for quantitative measurements, the effects of adding different amounts of acetylene to the flow on the signal need to be understood. Figure 5 shows the IR-LITGS signals recorded in nitrogen gas with different amounts of acetylene admixed. The signal characteristics that are commonly exploited to extract quantitative information about concentration include the oscillation period time of the acoustic contribution and the ratio of electrostrictive and

thermal contributions.²⁶ However, here we are interested in detecting small amounts of acetylene ($\ll 1\%$) in a gas flow. Admixing a small amount of acetylene to a buffer gas does not lead to measureable change in the speed of sound and, consequently, the oscillation period will remain constant within the measurement uncertainty. Moreover, as discussed above, the electrostrictive contribution to the signal is too weak to be observed. As an alternative, we calibrate the overall integrated signal intensity as a function of acetylene concentration. This is calculated by integrating the area under the signal curve from the time of the excitation pulse to the end of the measurement.

Figure 5: The IR-LITGS signals recorded with the OPO wavelength centered at 3256 cm^{-1} in a N_2 gas flow with different amounts of C_2H_2 admixed. The temporal profile of the mid-IR pump laser pulse represented by the Nd:YAG pump laser pulse is shown at time zero as a timescale reference.

Figure 6 plots the integrated IR-LITGS signal as a function of acetylene concentration. Panel (a) shows the signal recorded with the OPO tuned to the wavenumber 3256 cm^{-1} . The squares represent experimental data points showing a quadratic dependence on the concentration as expected.¹⁹ The error bars in the measurements are determined by a leave-one-out cross validation. Thus, they do

not only represent an estimation of how much the measurements deviate from the quadratic dependence, but also give an indication of the robustness of the calibration. The solid line is a best-fit quadratic function. The acetylene detection limit is estimated to be around 400 ppm. Panel (b) shows the concentration dependence of signals generated at wavelength 3229 cm^{-1} . The signals at this wavelength were found to be much stronger than at 3256 cm^{-1} , even though the absorption lines of C_2H_2 are weaker here. A possible reason is that the beam path difference between the two pump beams is less at this wavelength; however, calculations indicate that the path difference due to the difference in the refractive index of the compensating sapphire rod at the two wavelengths is $\sim 30\text{ }\mu\text{m}$. This should not have a large effect on the signal since the coherence length of the laser is $\sim 1\text{ mm}$. The overlap of the OPO modes and the C_2H_2 absorption lines could also be different at the different wavelengths. However, if this was the case, the signal should be strongly dependent on small changes in the OPO wavelength. Instead, the signal is more or less constant for small ($\sim 5\text{ cm}^{-1}$) wavelength changes and increases slowly and smoothly from 3256 cm^{-1} to 3229 cm^{-1} . This suggests that the OPO overlap with the C_2H_2 absorption lines is not significantly wavelength dependent, and that the signal increase is caused by something else. Different rovibrational levels are excited at the different wavelengths, which means that even though the absorption coefficient is lower, the amount of thermalized energy and the thermalization rate could be different, causing a stronger signal at 3229 cm^{-1} . The contrast of the oscillations for the signal at 3229 cm^{-1} is slightly larger (0.23) than the contrast at 3256 cm^{-1} (0.21). In principle, this can be interpreted in terms of a larger instantaneous energy transfer at 3229 cm^{-1} . However, the difference is fairly small and it should be noted that the broadband LITG excitation is generally not suitable for studying energy transfer mechanisms in detail as multiple lines are excited simultaneously. Hence, a detailed study of the energy transfer mechanisms in vibrationally excited C_2H_2 is beyond the scope of this work.

The detection limit at 3229 cm^{-1} , estimated by extrapolation of the quadratic fit to the concentration where the signal-to-noise ratio would be 1, is less than 300 ppm.

One way of improving the detection limit is to use a narrow-band or single-mode pump laser. Since the absorption of the pump laser beams would be more efficient for a narrow-band pump laser, the signal would be much stronger.

Figure 6: Concentration dependence of the IR-LITGS signal at 3256 cm^{-1} (a) and 3229 cm^{-1} (b).

The error bars are estimated from a leave-one-out cross validation.

Dependence on buffer gas

The thermalization process of LITGS is dominated by collisional effects and hence the buffer gas plays an important role. Figure 7 shows the IR-LITGS signal, recorded at OPO wavelength 3256 cm^{-1} , generated for 4145 ppm C_2H_2 diluted in four different buffer gases: Ar, N_2 , air, and CO_2 . The relevant thermophysical properties of these gases are given in Table 1. The measured quantities from the corresponding IR-LITGS signals are summarized in Table 2. The signal recorded in CO_2 shows significant differences compared to the other buffer gases. This is also reflected by the signal characteristics given in the table.

The IR-LITGS signal from C_2H_2 is more than two times higher in the CO_2 gas flow compared to the signals generated in the Ar, N_2 , or air flows. This is consistent with earlier infrared polarization spectroscopy (IRPS) experiments of the quenching rate of acetylene diluted in CO_2 and in N_2 , where the quenching of the signal was found to be much stronger in CO_2 than in N_2 .²⁷ The decay times of the Ar, N_2 , and air signals are quite similar, but the decay time of the signal in CO_2 is much longer. The exponential decay represents the decay of the stationary temperature grating, which is dependent on the thermal diffusion properties of the gas. As we can see in Table 1, the thermal diffusivity is very similar for Ar, N_2 and air but significantly lower for CO_2 . Thus, it is reasonable to have a slower decay in CO_2 compared to the other buffer gases.

The signal in CO_2 rises slower than the other signals. It peaks at $1.4\text{ }\mu\text{s}$ compared to $\sim 1\text{ }\mu\text{s}$ in the other buffer gases. Moreover, the contrast of the oscillations is much lower in CO_2 than in the other gases. The contrast is a measure of the relative strength of the temperature and acoustic gratings,⁸ showing that in CO_2 especially, the stationary part of the LITG is dominant. The slower rise of the signal in CO_2 combined with the low contrast shows that the rate of thermalization of the molecular internal energy is slower in CO_2 compared to the other gases. This indicates that the heat release

and internal energy transfer for C_2H_2 diluted in CO_2 happens by different mechanisms and hence on different time scales than in the other buffer gases.²⁸ As mentioned before, a detailed study of the energy transfer mechanisms between C_2H_2 and the different buffer gases is beyond the scope of this paper.

The oscillations disappear much faster in CO_2 compared to Ar, air, and N_2 ; the weak oscillations reappearing between 4 and 6 μs are not visible in the CO_2 signal. This may be interpreted as significantly stronger viscous damping in CO_2 . However, the exponential coefficient α in CO_2 is in the same order of magnitude as for nitrogen. Hence, the disappearance of the acoustic contribution is likely to be a result of the strongly enhanced and dominating stationary grating, which prevents the weak oscillations at longer delay times to be observed.

Figure 7: IR-LITGS signals generated in 4145 ppm C_2H_2 diluted in Ar, N_2 , air and CO_2 , respectively. The temporal profile of the mid-IR pump laser pulse represented by the Nd:YAG pump laser pulse is shown at time zero as a timescale reference.

The frequency of the oscillations in the signal is strongly dependent on the buffer gas. The oscillation frequency can be used to calculate the speed of sound in the different gases. Table 3 shows the measured oscillation frequencies (calculated using Fourier Transform analysis of the

signals) and the corresponding calculated speed of sound in the gas mixtures compared with reference values. The values for Ar, N₂ and air agree very well with the reference values, while for CO₂ the value is higher than expected. This difference could be caused by an increase in the temperature in the probe volume due to the efficient heat release; however, the temperature corresponding to the measured speed of sound in CO₂ would be 347 K. Assuming a probe volume of about 1 mm³ filled with CO₂, the energy required to heat it by 54 K is of the order of 50 μJ. This is about 0.6% of the pump laser energy. Multiplication of the OPO spectral profile and the C₂H₂ absorption spectrum in Fig. 2 indicates that this is a realistic value of the absorbed laser energy. Therefore, it can be concluded that the observed signal is a result of significant local heating. Nevertheless, it must be kept in mind that the same energy is absorbed in the other buffer gases as the absorption process itself is independent of the molecular environment of acetylene. The results, however, indicate that the collisional energy transfer from acetylene to the other gases is much less efficient. The discrepancy may be explained by different quenching mechanisms.

In Ar, N₂, and air, the signal rises faster and decays faster than in CO₂. A possible reason would be that Ar, N₂, and air can effectively take up vibrational energy from acetylene only when it is in the initially excited state, while CO₂ is a better quencher of lower lying levels that are reached at a later stage in the collisional de-excitation process and that possibly have longer life times. This explanation is slightly speculative and requires further investigation in the future.

Opportunities, uncertainties and possible problems

The oscillation frequency can be used to measure the temperature, if the gas composition is known, and vice versa.³ It is clear that the oscillation frequency for the IR-LITGS signal is strongly

dependent on the speed of sound, which in turn, for a specified gas mixture, depends on the temperature. In combustion environments, there are always large quantities of water vapor present, and H₂O has strong absorption lines in the mid-IR spectral region. This opens the possibility for temperature measurements using IR-LITGS from absorption of H₂O. However, in this case a mean molecular weight of the gas mixture needs to be fed into the calculation.

The largest error in the calculation of the speed of sound originates from determination and accuracy of the crossing angle between the beams.³⁰ For example, for the calculations here, a miscalculation of the crossing angle by 0.1° gives a 15 m/s error in the calculated speed of sound, which corresponds to a relative error of ~4.3%. Because of the difficulty in precise alignment of the invisible mid-IR laser beams, there is a relatively large uncertainty in the determination of the crossing angle. Performing a reverse calculation of the crossing angle using the reference values for the speed of sound of N₂, Ar, and air we obtain $\theta = 2.418^\circ$. Thus, the most straightforward approach for determining the experimental parameters is to carry out a calibration measurement in a gas with known temperature and gas composition.

Another factor, which can determine the accuracy of temperature measurements with IR-LITGS, is the grating spacing and the oscillation frequency, which are related as

$$f_{\text{osc}} = \frac{v_s}{\Lambda} = \frac{2v_s \sin\left(\frac{\theta}{2}\right)}{\lambda_{\text{pump}}} \quad (7)$$

It is clear that for the longer pump laser wavelengths in IR-LITGS, the oscillation frequency is lower compared to visible/UV wavelength LITGS signals created with the same crossing angle, meaning fewer oscillations can be completed before the acoustic waves leave the grating. The

accuracy of the measured oscillation frequency depends on the number of oscillations in the signal. In these measurements, the beam size in the direction of the acoustic wave propagation was ~ 2 mm. As an example, for a LITGS experiment with the alignment used in this article, if the pump beams are 0.4 mm wide, the oscillations would disappear after ~ 1 μ s, meaning the LITGS signal would only contain 4 oscillations at most. The choice of pump beam configuration in LITGS has been discussed in detail by Hemmerling et al.,⁶ with respect to efficient diffraction of the probe beam, the spatial resolution and a proper number of interference fringes in the signal. For efficient diffraction off the LITG, the requirement for Bragg diffraction must be fulfilled:

$$2\sqrt{2}(\lambda_{\text{probe}}/\lambda_{\text{pump}}) \cdot (w/\Lambda) > 1, \Leftrightarrow w/\Lambda > \frac{1}{2\sqrt{2}(\lambda_{\text{probe}}/\lambda_{\text{pump}})} \approx 2 \quad (8)$$

For probe wavelength 532 nm and pump wavelength 3.1 μ m, w needs to be at least two times larger than Λ . Assuming $w = m \cdot \Lambda$, where m is an integer > 2 , gives the following relations⁶

$$w^2 = \frac{\sqrt{2}m\lambda_{\text{pump}}d}{4}, \quad \tau_{\text{tr}}/T_{\text{a}} = \frac{m}{\sqrt{2}}, \quad \Lambda^2 = \frac{\sqrt{2}\lambda_{\text{pump}}d}{4m} \quad (9)$$

In the equations above, d is the length of the measurement volume. For a large number of oscillations in the signal, the transit time τ_{tr} needs to be a few times larger than the inter-fringe transit time T_{a} . Setting $m=10$ gives $\tau_{\text{tr}}/T_{\text{a}} \approx 7$, which should be enough to provide a good resolution of the oscillations. If the desired spatial resolution of $d=10$ mm for $\lambda_{\text{pump}}=3.1$ μ m, the pump beam geometry should be: $w \approx 0.33$ mm, $\Lambda \approx 33$ μ m, crossing angle $\theta \approx 5.4^\circ$, $T_{\text{a}} \approx 96$ ns and $\tau_{\text{tr}} \approx 680$ ns.

Conclusions

We have shown efficient generation of thermal IR-LITGS signals in room temperature, atmospheric pressure gas flows containing C_2H_2 using pump radiation around $3\ \mu m$. The low contrast of the oscillations in the IR-LITGS signal and the slowly varying “hump” shows that the thermalization of the absorbed laser energy is not instantaneous, but rather slow compared to the oscillation period.²¹ The relatively large grating spacing combined with the thermal diffusivity of the gases contributes to the relatively slow signal decay. The signal strength is found to be proportional to the square of the C_2H_2 concentration, as expected from LITGS theory,¹⁹ indicating the possibility of IR-LITGS for quantitative concentration measurements of species with absorption lines in the mid-IR spectral region. A detection limit of less than 300 ppm was estimated from experiments with systematically varied concentration. There is a lot of room to improve the detection limit. The use of a probe laser with higher output energy can increase the signal since the signal is proportional to the probe laser intensity. Solid state cw lasers, with output powers up to 4 W, are commercially available at reasonable costs. Heterodyne detection of the signal may be another option to enhance the signal levels.^{31,32} Using a single mode IR laser as a pump laser is expected to greatly enhance the signals as well, since it can be tuned to a single strong absorption line and hence a large fraction of the laser energy can be absorbed. Scanning the wavelength of a narrowband IR laser across the CH stretching region of the spectrum will also enable multi-species measurements and the analysis of more complex gas mixtures. The difference in line positions and signal intensities of different spectroscopic lines for different molecules can be measured and used, for example, for relative concentration measurements. High-resolution LITGS using a narrowband excitation laser also enables a more detailed study of relaxation mechanisms for different species and/or different spectral lines in one species.

The signals generated with CO₂ as buffer gas were more than twice as strong as the signals in Ar, N₂ and air, due to more efficient quenching and thus more efficient collisional energy transfer in CO₂. The oscillation frequency of the acoustic signal contribution is dependent on the speed of sound of the gas mixture. For Ar, N₂ and air the determined values of the speed of sound were in excellent agreement with reference values from the literature. For CO₂ a large discrepancy was observed. The speed of sound indicated an elevated temperature in CO₂. This can be explained by a large amount of energy released through collisional quenching. However, further work is required to unravel the phenomenon in detail.

There is a promising potential for IR-LITGS temperature measurements in combustion environments, where the strong absorption lines of H₂O in the mid-IR spectral region can be used for resonant LITGS generation. Careful alignment or a calibration measurement will be necessary to reduce the uncertainty of the temperature measurement due to the uncertainty of the crossing angle of the pump beams, and due to the uncertainty resulting from the complex composition of the gas mixture in a reacting flow. Care must also be taken when selecting the pump beam crossing angle, since a large number of oscillations is needed before the acoustic waves travel out of the interaction region in order to get accurate and precise temperature measurements.

In conclusion, the potential of IR-LITGS in the gas phase using an infrared OPO with wavelengths around 3 μm has been successfully demonstrated. A key benefit of the technique is that it enables spectroscopy and detection of IR-active molecules in the mid-infrared spectral range with signal detection in the visible spectrum. Hence, the strong absorption bands of the fundamental vibrational modes combined with the sensitive detectors in the visible spectrum can facilitate ultrahigh detection sensitivity of trace species in the future. Moreover, it was demonstrated that IR-LITGS is a suitable technique for studying molecular physics phenomena in gases.

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Table 1: Physical constants for the different buffer gases at standard conditions (296 K and 1 atm).²⁹

	Thermal diffusivity / mm ² /s	Specific heat capacity, c_p / kJ/kg·K	Density / kg/m ³	Dynamic viscosity / μPa*s
Ar	20.3	0.522	1.65	22.4
N₂	21.4	1.04	1.15	17.7
Air	21.3	1.005	1.20	19.8
CO₂	10.7	0.849	1.82	14.8

Table 2: Different properties of the IR-LITGS signal created in different buffer gas.

Buffer gas	Integrated signal strength /Arbitr. units	Exponential decay time /μs	Contrast of first oscillation
Ar	7.9	3.53	0.24
N₂	7.2	3.40	0.21
Air	6.7	3.39	0.21
CO₂	18	5.02	0.02

Table 3: The oscillation frequency in different buffer gas and the corresponding calculated speed of sound, compared with reference measurements of the speed of sound.

Buffer gas	Oscillation frequency /MHz	Speed of sound /(m/s)	Reference²⁹ speed of sound at 20° C /(m/s)	Difference from reference speed of sound /(m/s)
Ar	4.4	320	319	1
N ₂	4.8	349	349	0
Air	4.7	342	343	-1
CO ₂	4.0	291	267	24