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Broadband cantilever-enhanced photoacoustic spectroscopy in the mid-IR using a supercontinuum

TOMMI MIKKONEN^{1,*}, CAROLINE AMIOT^{1,2}, ANTTI AALTO¹, KIM PATOKOSKI¹, GOËRY GENTY¹, AND JUHA TOIVONEN¹

¹Laboratory of Photonics, Tampere University of Technology, Tampere, Finland

²Institut FEMTO-ST, UMR 6174 CNRS, Université de Bourgogne Franche-Comté, Besançon, France

*Corresponding author: tommi.j.mikkonen@tut.fi

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We demonstrate cantilever-enhanced photoacoustic spectroscopy in the mid-infrared using a supercontinuum source. The approach is broadband and allows for higher photoacoustic signal intensity and enhanced signal-to-noise ratio as compared to systems employing conventional back body radiation sources. Using this technique, we perform spectroscopic measurements of the full ro-vibrational band structure of water vapor at 1900 nm and methane at 3300 nm with relative signal enhancement factors of 70 and 19, respectively, when compared to measurements that use a black body radiation source. Our results offer novel perspective for photoacoustic detection opening the door to sensitive broadband analyzers in the mid-infrared spectral region.

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Photoacoustic spectroscopy (PAS) is an optical sensing technique that detects the pressure wave resulting from local heating and thermal expansion when light is absorbed by a gas sample placed inside an acoustic cell. Photoacoustic spectroscopy with high-power lasers is particularly attractive as the signal detected by a pressure-sensitive detector is directly proportional to the absorbed light power, resulting in highly sensitive background-free measurements. Another significant advantage of PAS is the small volume of gas sample required which makes it generally more compact than e.g. conventional Fourier transform infrared spectrometers (FTIRs) [1]. Microphones with electrical readout are commonly used as detectors in PAS, however their sensitivity is limited by the electrical noise. Resonant acoustic cells are therefore often needed for high sensitivity measurements, which limits the detection to a single modulation frequency. By replacing the microphone with a micromechanical cantilever whose mechanical oscillations are detected with an optical interferometer, acoustic resonance enhancement is not required, either from the cell or from the cantilever, allowing for broadband detection with similar sensitivities [2] and indeed sub-ppt sensitivities have been reported using such a cantilever enhanced photoacoustic spectroscopy approach (CEPAS) [3].

Various types of light sources have been used in laser based PAS systems, including distributed feedback diode lasers [4, 5] and external cavity diode lasers [6] in the near-infrared, or quantum cascade laser [7, 8] and optical parametric oscillators [9] in the mid-infrared. These sources are inherently narrowband or they have a limited wavelength-tuning range. Broadband detection may be achieved using thermal emitters or black body radiators [1, 10] but their low brightness limits the sensitivity in this case. Supercontinuum (SC) sources on the other hand can exhibit extremely broad bandwidth with brightness exceeding by orders of magnitude that of thermal emitters and the unique properties of SC sources have made them ideal light sources candidates for many sensing and imaging applications including spectroscopy, microscopy or optical coherence tomography [11–15]. In this Letter, combining a broadband supercontinuum source with FTIR CEPAS, we demonstrate sensitive, broadband photoacoustic detection of water vapor and methane in the mid-infrared spectral region. Our results show a significant increase in the signal intensity as compared to when using a thermal emitter. A significant advantage of the fiber-based SC source is its high spatial coherence allowing for (1) a much larger power spectral density in the FTIR as compared to blackbody radiators and (2) adjustment of the FTIR beam path and tuning the resolution of the measurement. Our results open up new perspectives for gas sensing and, more generally, spectroscopic applications using broadband photoacoustic detection.

Our experimental setup is shown in Fig. 1. The supercontinuum source is generated by injecting 0.6 ns pulses at 1547 nm from a gain-switched fiber laser (Keopsys-PEFL-K09) with tunable repetition rate into the anomalous dispersion regime of a 4-m-long silica dispersion-shifted fiber (DSF, Corning Inc LEAF) followed by an 8 m long fluoride fiber (ZBLAN) as described in [12]. Here, depending on the gas sample to be characterized, we used different repetition rate for the pump laser so as to optimize the power spectral density of the SC in the spectral range of interest. Specifically, for a repetition rate of 70 kHz, the 10 kW peak power of the pump laser pulses leads to the generation of a broadband SC extending from c.a. 1500 nm up to c.a. 3700 nm as the result of multiple cascaded nonlinear dynamics including modulation instability, soliton formation and Raman self-frequency shift [16]. When the repetition rate is increased

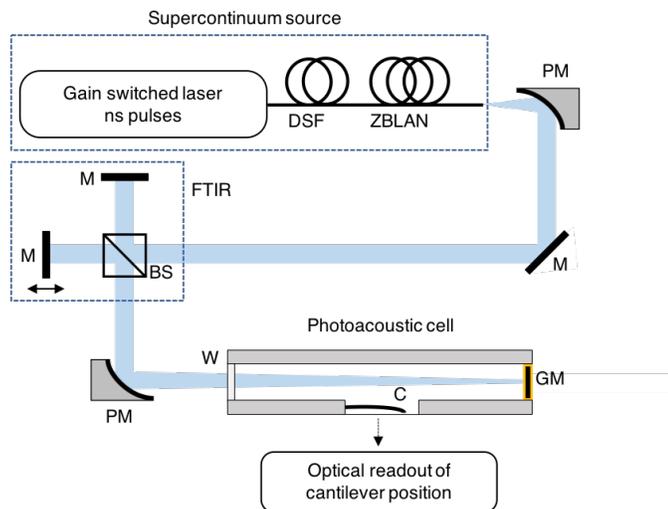


Fig. 1. Experimental setup. PM, off-axis parabolic mirror; M, mirror; BS, beam splitter; W, window; GM, gold mirror; C, cantilever.

to 400 kHz, the peak power of the pump pulses is reduced to less than 2 kW and the spectrum extends from 1500 nm up to 2400 nm. The average SC spectra measured with a scanning monochromator and corresponding to 70 kHz and 400 kHz repetition rates for the pump laser are shown in Fig. 2 as the blue and red solid lines, respectively. Note that in the 70 kHz repetition rate case, the short wavelengths side of the SC spectrum was limited using a long-pass filter (Northumbria Optical Coating, SLWP-2337) with a cut-on wavelength of 2300 nm. The spectral filter was used to remove the excess noise of the SC source in the 1900 nm band at a lower repetition rate. Note that the sharp features observed at around 2600 nm in the average spectrum obtained for a 70 kHz repetition rate are caused by water vapor absorption present in air. A half-a-meter monochromator (Spectral Products DK480 1/2) was used to measure the SC spectra with a maximal resolution of 1 nm, and a lock-in amplifier (PerkinElmer 7225) was used to increase the signal-to-noise ratio (SNR).

Light from the SC is collimated into a 2 mm (diameter) beam using a silver reflective collimator and sent to a scanning FTIR interferometer (Bruker IRCube) modulating the spectrum of the light source. For comparison, we also perform reference measurements that use a black body source having a beam diameter of 25 mm are performed with the same FTIR instrument. The order of magnitude smaller beam size of the collimated SC source demonstrates the future potential in miniaturizing the FTIR scanning instrument when used with a spatially coherent light source. At the FTIR output the beam is focused with a parabolic mirror ($f = 76.2$ mm) into a non-resonant photoacoustic cell (Gasera) that contains the gas sample to be measured. The cell is gold-coated, 10 cm long and 4.5 mm diameter corresponding to a sample volume smaller than 8 mL. The windows of the cell are made of BaF₂ and a gold coated mirror is placed right after the back window enabling the optical path length to be increased by a factor of two. Note that the same dual-path cell arrangement was used in all the measurements presented below. The temperature and pressure of the cell were set to 50 °C and 1 bar, respectively. The pressure changes inside the cell caused by light absorption in the gas sample are read optically

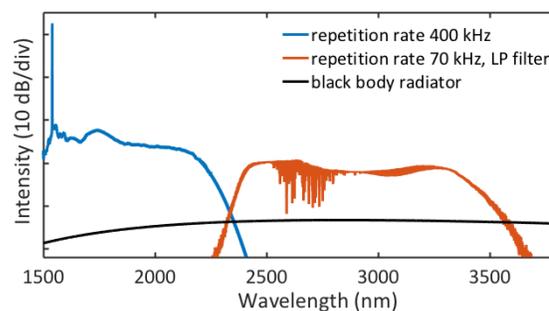


Fig. 2. Supercontinuum spectra corresponding to pump laser repetition rates of 70 kHz (solid red line) and 400 kHz (solid blue line) and used for the photoacoustic spectroscopic measurements of methane and water vapor, respectively. Note that the SC spectrum corresponding to 70 kHz has been spectrally filtered with a long-pass filter with cut-on wavelength of 2300 nm. The spectrum of the black body radiation source is theoretically estimated based on the temperature of the IR radiator (solid black line)

via interferometric detection where a cantilever acts as a moving mirror whose mechanical oscillations change the period of the interference fringes (see Ref. [17] for details on the readout procedure). The cantilever is gold-coated with dimensions of 6 mm, 10 μ m, and 1.5 mm (length, thickness, and width, respectively). The FTIR scanning mirror velocity was 1.6 kHz monitored by a HeNe laser. The modulation frequencies for the considered mid-infrared wavelength range of 1.7–3.5 μ m correspond to 600–290 Hz at the optimal frequency range for the CEPAS cell. The gas sample absorption spectrum is obtained by the Fourier transform of the recorded interferogram. The minimum wavelength resolution of the instrument is determined by the FTIR maximum optical path difference of 1 cm.

The experimentally recorded absorption spectrum of normal room air (20 °C, RH 30 %) water vapor with 7000 ppm concentration in the PAS cell and using the SC source with a repetition of 400 kHz as described above is shown in Fig. 3 (solid blue line). The total SC average power was 414 mW with a power spectral density of 275 μ W/nm in the water vapor absorption band, out of which 40 % was inserted into the CEPAS cell after the FTIR. The spectrum was measured with 1.4 nm resolution and averaged over 10 scans for a total measurement time of 50 s. We observe excellent correspondence with the theoretical spectrum predicted from the HITRAN database (plotted as a mirror image in the figure). For comparison, we also repeated the experiment using a black body radiation source (see the solid black line in Fig. 2 for an illustration of the spectrum). Note that the photoacoustic signal using the black body source has been magnified 10 times in the figure for visualization purposes, showing that the SC yields far better performance in terms of sensitivity and SNR. More specifically, the signal intensity and SNR are increased by a factor of 70 and 13, respectively, when using the SC source.

We then used the spectrally filtered SC source with 70 kHz repetition rate to measure the mid-infrared ro-vibrational absorption band of methane sampled from a flow of premixed 400 ppm methane in nitrogen carrier gas. The SC total power in this case (after the filter) was 78 mW with a power spectral

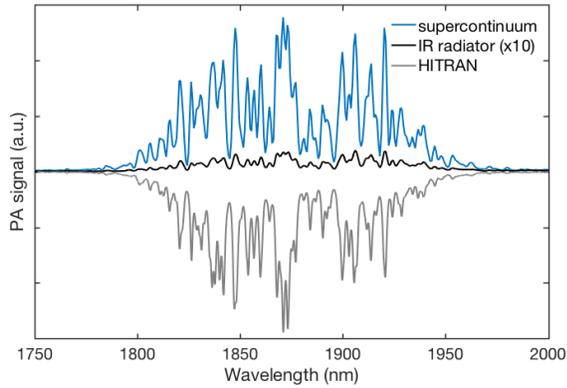


Fig. 3. Experimentally measured absorption spectrum of water vapor with the supercontinuum (solid blue line) and black body source (solid black line). The measurement resolution is 1.4 nm and the spectrum averaged over 10 different scans. The theoretical absorption spectrum as predicted from the HITRAN database is shown as the mirror image (solid grey line). Note that the results obtained with the black body have been magnified by 10 for convenient visualization.

density of $71 \mu\text{W}/\text{nm}$ in the absorption band of methane. Again, 40 % of this power was finally injected into the CEPAS cell. The results are shown in Fig. 4 (red solid line), where we find excellent agreement with the absorption spectrum predicted from HITRAN. The results from the black body radiation source are also shown in the figure (with a 5 times magnification). As in the case of the water vapor, it is clear that the signal measured when using the SC is significantly increased (19 times), as compared to that obtained with the black body source. However, the increase in the SNR is only 1.8 times in this case, which is due to increased noise in the SC source at reduced repetition rate. Indeed, there are significant pulse-to-pulse fluctuations in the SC spectrum caused by the initial stage of modulation instability in the SC generating nonlinear dynamics [16], and a lower repetition rate results in an increase in the noise level as the intensity recorded is then averaged over a reduced number of SC pulses for lower repetition rates.

Besides the increase in the detected signal strength when using the SC source, another significant advantage as compared to a standard black body source lies in the fact that the SC is perfectly spatially coherent and the beam remains collimated independently of the optical path difference used in the FTIR. This means that one can increase the measurement resolution without any line-broadening or shifting effects [18] and still maintain high signal intensity. This is illustrated in Fig. 5 where we show the measured absorption spectrum of methane with different resolutions. The measurement times for resolutions of 1, 2 and 4 nm were 200 s, 100 s, and 50 s, respectively, with corresponding achieved SNRs of 136, 221, and 278. One can see how the lines become sharper and the signal amplitude is increased for higher resolutions. This contrasts with the use of a spatially incoherent black body source which requires reducing the input aperture size to ensure reasonable collimation over larger distances, thus leading to decreased signal intensities when performing measurements at higher resolutions.

We evaluated the concentration detection limits (3σ , 50 s) to be 2.6 ppm and 1.4 ppm for the black body and SC sources, respectively. The noise level was estimated from the non-absorbing

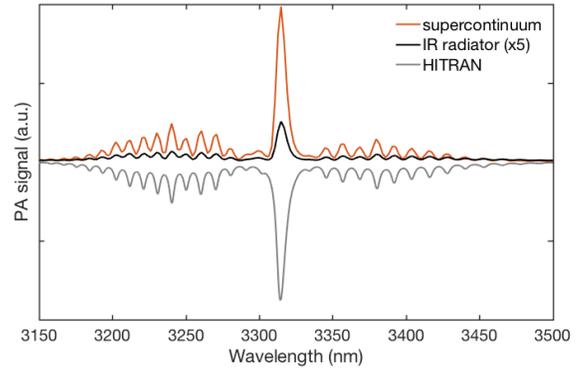


Fig. 4. Experimentally measured absorption spectrum of 400 ppm methane with the supercontinuum (solid red line) and black body source (solid black line). The measurement resolution is 4 nm, and the spectrum averaged over 10 different scans. The theoretical absorption spectrum as predicted from the HITRAN database is shown as the mirror image (solid grey line). Note that the results obtained with the black body have been magnified by 5 for convenient visualization.

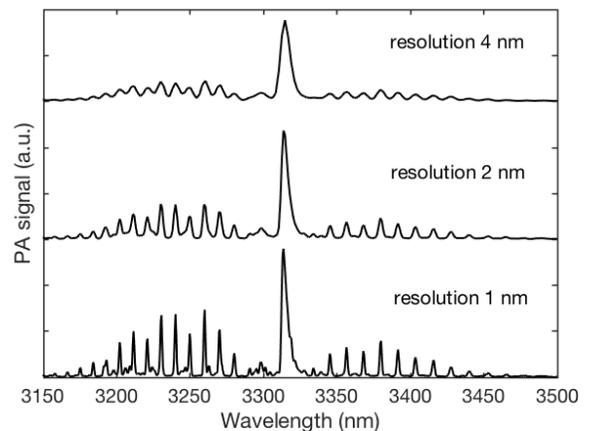


Fig. 5. Measured absorption spectrum of methane for different FTIR resolutions as indicated. The measurement time is inversely proportional to the resolution. The measurement times for resolutions of 1, 2, and 4 nm are 200 s, 100 s, and 50 s, respectively, with corresponding achieved SNRs of 136, 221, and 278.

part of the spectrum without methane by dividing the area to 10 blocks each consisting of 10 data points and averaging the standard deviations. The strongest signal value was then compared to the noise level (3σ). The limit of detection was calculated by dividing the concentration by the SNR. The rather low enhancement in the detection limit when using the SC is caused by the high intensity noise level of the supercontinuum source induced by large pulse-to-pulse fluctuations. We anticipate that lower detection limits can be achieved using e.g., a more stable SC source with even higher power spectral density, a resonant acoustic cell, and single-frequency detection, or with a larger measurement setup. Yet, one should consider the detection limits achieved here in the context of broadband measurement from a small sample volume.

We have performed broadband CEPAS using a supercontinuum light source and demonstrated the potential of the technique by measuring the absorption spectrum of water vapor and methane in the mid-infrared spectral region. The approach allows for significant improvement in terms of sensitivity and resolution as compared to the use of a conventional black body radiation source. The spatially coherent and collimated SC beam also enables miniaturization of the Fourier transform spectrometer, as the narrow beam can easily be guided even in a small-form-factor instrument. Furthermore, high spatial coherence, in principle, enables multi-pass arrangements through the PAS cell, which could lead to enhanced sensitivity. Lower detection limits may be reached by reducing the intensity noise of the supercontinuum source using for example pump pulses of shorter durations and/or increasing the power spectral density of the supercontinuum source. The measurement time, on the other hand, is mostly limited by the cantilever frequency response which imposes the use of a low scanning speed FTIR. Yet, using a shot-to-shot stable SC source would allow for single scan measurements and improve the measurement speed by an order of magnitude. Our results open up novel perspectives for the development of cost-effective apparatus for broadband gas sensing.

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