Sensitive wavelength-modulated photoacoustic spectroscopy with a pulsed optical parametric oscillator

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With a laser-excited acoustic wave as the carrier wave and by modulation of the light wavelength of a multikilohertz-repetition-rate optical parametric oscillator at a lower frequency than the acoustic frequency, we demonstrate a wavelength–amplitude double-modulation technique and achieve an enhancement factor of 35 in sensitivity in photoacoustic trace gas detection with the technique.

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Photoacoustic spectroscopy has one of the highest sensitivities among various techniques in trace gas detection. It has therefore become an important tool in air pollution monitoring, the detection of volatile organic compounds, industrial process control, and the tracking of toxic and explosive gases.[1] In the past 10–15 years the optical parametric oscillator (OPO), because of its broad wavelength coverage and its high peak power, has become an important light source for sensitive gas detection with photoacoustic spectroscopy.[1,2] In the meantime the technique of wavelength modulation (WM) and its close analog, frequency modulation,[3–8] have often been employed in absorption spectroscopy of trace gases since the technique is effective in suppressing the baseline caused by the light source and the detector. There is therefore an obvious advantage in gaining detection sensitivity by use of WM with an OPO. However, to our knowledge, until now the technique of WM has not been incorporated into the OPO, whether it is cw or pulsed. One reason for this could be that modulating the wavelength of an OPO is not as easy as it is for a diode laser.[9] In conventional WM the carrier frequency is the optical frequency, and the modulation frequency ranges from the kilohertz to the microwave or the gigahertz region. Since the OPO is based on instantaneous nonlinear interaction of the pump beam with the medium, controlled modulation of the optical frequency can be a tricky task. In this Letter we show that instead of directly modulating the wavelength within each light pulse, it is possible to employ a wavelength modulation–amplitude modulation (WM–AM) technique, with the acoustic wave generated by light absorption as the carrier wave and modulating the OPO light wavelength at a lower frequency than the acoustic frequency to produce in photoacoustic spectroscopy similar differential spectra and baseline suppression effects as obtained in conventional WM spectroscopy.

We consider an OPO whose output is a pulse train with a pulse repetition frequency at the acoustic frequency ω_a. If we modulate simultaneously the wavelength of the OPO output with a sinusoid at a frequency $\omega_m < \omega_a$ with modulation amplitude Δv, the acoustic signal produced by an absorbing gas can be represented by[9,10]

$$U(v_{\mathrm{opo}}, t) = P\Big\{[A\alpha(v_{\mathrm{opo}}) + B\cos(\varphi_b)] + A'\Delta v\,\frac{\partial\alpha(v_{\mathrm{opo}})}{\partial v}\cos(\omega_m t)\Big\} \times \exp(-i\omega_a t) + N\,, \tag{1}$$

where $U(v_{\mathrm{opo}}, t)$ is the photoacoustic signal that is in phase with the absorption signal, α is the absorption coefficient of the gas, v_{opo} is the OPO frequency, P is the peak output power, $\partial\alpha/\partial v$ is the partial derivative of α with respect to v, ω_a is the acoustic frequency, and φ_b is the phase difference between the background and the signal caused by sample absorption. Furthermore, A and A' are system-dependent proportionality constants, B is the amplitude of the background, and N is the noise not related to laser radiation. Here P and B are assumed to be slowly varying quantities in v.

Equation (1) describes an acoustic signal of frequency ω_a whose amplitude has a dc component and an ac component at ω_m. Extracting only the ac component allows a background-free derivative spectrum for α to be obtained. This WM–AM double-modulation technique can be realized with a multikilohertz-repetition-rate OPO. The experimental setup is shown in Fig. 1. The OPO used was an improved version of the OPO reported previously.[11] In this newer version the pump beam was introduced into the OPO cavity by use of a 45° dichroic mirror (highly reflecting at 1064 nm and highly transmitting at $\lambda > 1.4\ \mu$m).[12] Hence the OPO could be operated over the entire tuning range (1.45–4.0 μm) with a single set of optics. The grating used in Ref. 11 was replaced by a 50-mm-wide grating that has 300 grooves/mm blazed at 3.0 μm. This grating permitted the idler wavelength to resonate in the cavity. In addition,

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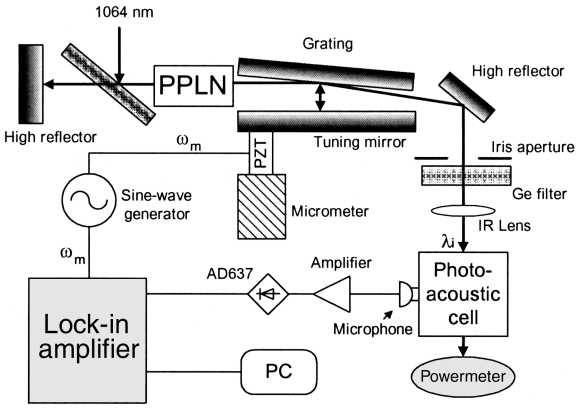

Fig. 1. Schematic of the OPO, modulation scheme, and detection setup. The OPO cavity was embedded between a high reflector and the tuning mirror. The periodically poled lithium niobate (PPLN) crystal was held in a temperature-stabilized (±0.1 °C) oven. WM was achieved with a piezoelectric crystal (PZT) attached to the tuning mirror and driven by a sine-wave generator. The acoustic signal was detected by a microphone, amplified, rectified (AD637), and then processed by a phase-sensitive lock-in amplifier.

an iris aperture was placed 10 cm from the grating output position and adjusted to transmit only the central portion of the IR beam. The function of the iris was to cut off the off-axis output radiation, which was found to be the major contributor to a broad pedestal and some broadening of the primary bandwidth of the output spectrum observed in Ref. 11. The broadening was the result of off-axis phase matching caused by the pump beam, which was not a perfect plane wave. Implementation of the wider grating, a larger pump beam size of 250 μm, and the iris aperture resulted in a threefold reduction of the OPO output bandwidth. When pumped by 4 W of 1064-nm radiation at 4 kHz, this OPO produced 60–100-mW output in the 3.0-μm region with a FWHM bandwidth of typically ~0.1 cm^{-1}.[13] The output wavelength, being fixed by the grating, was stable for at least several hours to within 20% of the output bandwidth, whereas the average power was stable to better than 5%.

Wavelength tuning was accomplished with a stepping motor connected to the tuning mirror. In the present experiments the OPO was tuned to an isolated absorption line of methane near 3086 cm^{-1}. To modulate the wavelength, a piezoelectric crystal was attached to the tuning mirror. A sinusoidal voltage was applied to the piezoelectric crystal to dither the mirror in the tuning direction at a modulation frequency of ω_m = 31.5 Hz. The carrier frequency ω_a was equal to the pulse repetition rate of the OPO (4 kHz). The magnitude of the sinusoidal voltage was adjusted during the experiment to give the largest demodulated signal. The IR output was focused into a differential photoacoustic cell through which a mixture of 1 part per million by volume (ppmv) methane in nitrogen flowed at a rate of 60 cm^3/min. The cell was carefully aligned to minimize the background photoacoustic signal. The 4-kHz acoustic signal detected with an electret microphone was first amplified and then rectified by a true rms detector (Analog Devices AD637), followed by a low-pass filter to extract its ac component. The output was then measured with a phase-sensitive lock-in amplifier synchronized to ω_m with a time constant of 1 s.

Figure 2 shows in logarithmic scale the photoacoustic spectrum and a corresponding background signal spectrum obtained without WM. The background trace was recorded by flushing the photoacoustic cell with pure nitrogen. The line profile shown matches well to the line profile calculated from HITRAN for 1 ppmv methane and 25 ppmv water vapor in nitrogen and convoluted to the laser line shape.[14] The presence of water vapor in the cell was incidental. When WM was applied, a derivative spectrum was obtained. This can be seen in Fig. 3. The background signal is now reduced to below the noise level. The peak-to-peak amplitude (89 ± 3 μV) of the differential line profile is approximately one third of the peak amplitude (260 ± 5 μV) presented in Fig. 2. In Fig. 4 the WM spectrum of Fig. 3 is compared with the derivative spectra calculated from the HITRAN

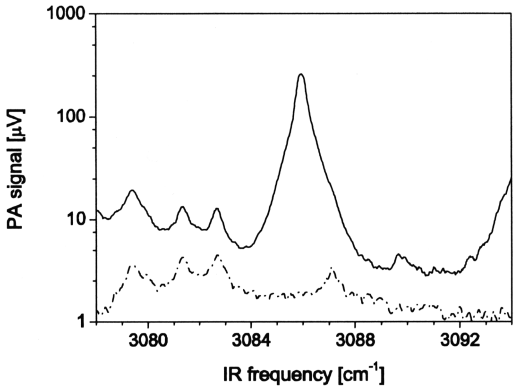

Fig. 2. Photoacoustic spectrum obtained without wavelength modulation: solid curve, 1-ppmv methane in nitrogen; dashed curve, pure nitrogen. The main peak is due to methane. The smaller peaks are assigned to water vapor either from the methane mixture or residual in the cell. The vertical axis is given in a logarithmic scale to show the magnitude of the background.

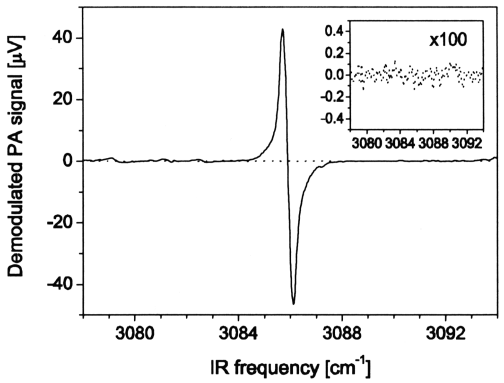

Fig. 3. Derivative spectrum obtained after demodulating the photoacoustic signal: solid curve, 1-ppmv methane in nitrogen; dotted line, pure nitrogen. The inset, with the vertical scale amplified 100 times, shows the magnitude of the pure nitrogen signal.

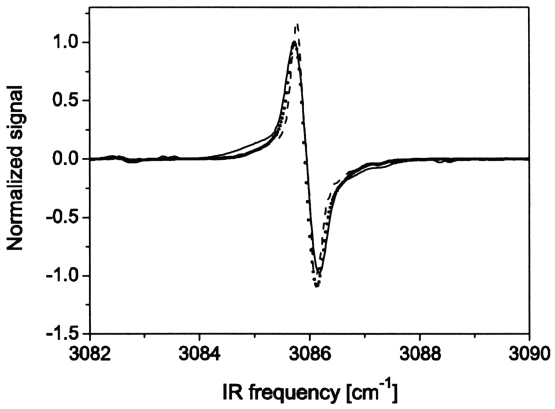

Fig. 4. Comparison of methane line spectra obtained from this experiment (dotted curve), derivative of the spectrum given in Fig. 2 (dashed curve), and derivative of the methane line simulated from HITRAN (solid curve).

spectrum and from the AM spectrum of Fig. 2. The agreement among all three traces shows that the technique of WM–AM works and can be described by the theoretical model resulting in Eq. (1).

The proof of the advantages of the WM–AM technique can be seen in the detection sensitivity. Without WM the sensitivity is limited by the presence of the background signal. This background, taken for the best situation for this case to be the 3090.5–3092-cm^{-1} region, where no water absorption takes place, is approximately 1.24 ± 0.2 μV, which is in agreement with values reported previously.[15] Since the photoacoustic signal peaks at 260 μV, this results in a signal-to-background ratio of 210. With WM the measured background is reduced to the noise level, which is 0.053 μV. For the peak-to-peak amplitude of 89 μV we obtained a signal-to-noise ratio of 1679. This is a factor-of-8 improvement over the AM case. This enhancement factor is in line with enhancement factors reported for other WM experiments with laser sources.[3,4]

The advantages of the WM–AM technique are most prominent in applications in which a large background is present, such as in multipass configurations in which the laser beam hits the cell windows or the reflecting mirrors many times and produces a large background signal. To demonstrate this advantage, we used a pair of mirrors to reflect the IR beam a multiple number of times through the photoacoustic cell. Taking losses at the mirrors and the windows into account, we estimated that this multipass scheme would provide a theoretical signal enhancement of 14. Without WM the signal enhancement was completely offset by a corresponding increase in the background signal that originated from the mirrors and the windows. With WM the background increased by a factor of 2.18 to a value of 0.116 μV because of beam clipping inside the cell, whereas the signal increased by a factor of 9.54 (theoretical maximum is 14). The resulting overall signal-to-noise ratio measured with this multipass cell was 7358. This is a gain of 35 over the single-pass AM case. It implies a detection sensitivity of 136 parts in 10^{12} for methane, which is one of the highest reported sensitivities reached for photoacoustic methane detection.[16] The equivalent absorption sensitivity of 3.7×10^{-10} $cm^{-1}\,W\,Hz^{-1/2}$ is comparable with that obtained by cavity ringdown spectroscopy when corrected for similar experimental conditions.[17] Since the background and signal amplitudes are still off from their optimal values, there is room for further improvement. It is also important to note that the enhancement demonstrated here was accomplished in the presence of interfering species in the form of nearby water transitions.

Absorption spectroscopy measures the depletion of laser power. The large signal from the laser power makes it necessary to employ high-frequency modulation to shift the detection away from the amplitude noise of the laser. In contrast, WM photoacoustic detection is a detection method with zero or very low background. Hence even low-frequency modulation, as used in these experiments has produced good results. Consequently, high-frequency electronics are not needed to implement this approach. Finally, this method of WM–AM of the OPO should also work in direct absorption and cavity ringdown spectroscopy measurements.

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