Reduced-background gas-phase absorption spectroscopy

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Received April 6, 1998

We propose and demonstrate a new method for single-shot multiplex absorption spectroscopy that permits enhanced sensitivity in the simultaneous measurement of multiple spectral lines in rapidly changing gas-phase media, such as turbulent flames. It uses an ultrashort laser pulse that propagates through the absorbing medium, for which the relevant absorption information resides in the free-induction decay that is trailing behind the transmitted pulse. Time gating out most of the transmitted pulse, but not the free-induction decay, enhances the relative fraction of light that contains absorption information when the spectrum is measured. This procedure reduces the background associated with the input light, thus enhancing detection sensitivity. © 1998 Optical Society of America

OCIS codes: 300.1030, 320.7160, 320.7120, 320.7100, 320.7110.

Sensitive absorption spectroscopies can detect trace-gas species. Unfortunately, current methods, such as frequency-modulation,[1] Fourier-transform,[2] cavity ringdown,[3] multiphoton ionization,[4] and photoacoustic[5] spectroscopies, all require scanning in either time or frequency for an entire spectrum to be achieved. As a result, in turbulent environments, such as combustion or the atmosphere, where species concentrations and temperature can vary rapidly compared with scan times, these methods yield only time-averaged spectra. Therefore, a rapid (e.g., single-shot) sensitive technique is highly desirable.

Once could obtain a single-shot absorption spectrum simply by sending a burst of broadband white light through the absorbing medium and then measuring the transmitted-light spectrum. Unfortunately, such a simple method has limited sensitivity because of the large (and noisy) background spectrum of the unabsorbed input light upon which the absorption dips sit. The finite dynamic range of any detector limits the total amount of light incident upon the detector, and hence the measurement sensitivity. Worse, noise associated with both the input spectrum (especially for broadband incoherent light) and the detector response (e.g., pixel-to-pixel variation in a CCD) reduces sensitivity further.

If we could reduce this background—without significantly reducing the absorption dips—we could enhance sensitivity. Ordinary incoherent background subtraction—measuring the spectrum both before and after the medium and subtracting the background—generally does not help. One could achieve coherent optical subtraction interferometrically, e.g., by placing the sample in one arm of a Mach–Zehnder interferometer and adjusting the optical path difference to π for all wavelengths such that the difference between the electric fields in the two arms is measured at the output. Unfortunately, this method fails because of the practical difficulties associated with interferometers, the most serious of which is their extreme sensitivity to small optical path difference fluctuations, which is unfortunately most detrimental when a single-shot method is most desired, e.g., in a turbulent medium such as a flame.

Here we describe an alternative coherent subtraction technique, which we call femtosecond augmented-signal time-gated absorption spectroscopy (FASTGAS). FASTGAS involves temporally separating the background from the absorption information by using an ultrashort laser pulse as the input. When an ultrashort pulse traverses an absorbing medium, the medium continues to radiate coherently for a time determined by its polarization dephasing time (T_2). This free-induction decay (FID) contains the absorption information[6]; in fact, it is the time-domain Fourier transform of the complex absorption spectrum. For weakly absorbing samples most of the incident light remains in the short input pulse, which appears as the background in the spectrum. FASTGAS involves temporally gating out the transmitted input pulse so that only the FID, whose spectrum represents the sample absorption, remains. Figure 1 illustrates this principle. (Note that it is also possible to time resolve the FID and obtain the absorption spectrum from its Fourier transform,[7] but this method requires scanning.)

Another picture of FASTGAS involves realizing that absorption spectroscopy is a type of optical

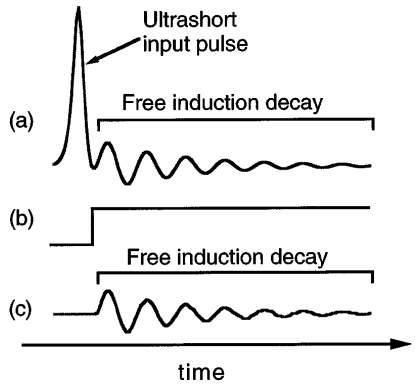

Fig. 1. (a) Electric field envelope of a pulse after passage through an absorbing medium with two absorption lines (b) transmission through an ideal gate, (c) transmitted electric field through the gate. Note that the magnitude of the FID is greatly exaggerated compared with the pulse amplitude in (a).

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heterodyne detection in which the unabsorbed light field, $E(\omega)$, acts as a local oscillator (LO) for the weaker FID signal, $i\chi(\omega)E(\omega)$. The transmitted-light spectrum is $I_{\text{trans}}(\omega) = |E(\omega) + i\chi(\omega)E(\omega)|^2 \approx |E(\omega)|^2 - 2\,\text{Im}[\chi(\omega)]\,|E(\omega)|^2$, and the resultant signal-to-background ratio is $2\,\text{Im}[\chi(\omega)]$. For weak absorptions, however, the LO is typically much stronger than the FID signal. In this case the signal-to-noise ratio is far from optimal.[8] Therefore, reducing the strength of the LO (i.e., the input pulse) will improve sensitivity. On the other hand, it is generally best not to remove all the LO to avoid measuring the square of a small signal $|\chi(\omega)E(\omega)|^2$. Allowing a small portion of the LO to remain to mix with and thus to amplify the FID achieves optimum sensitivity.[8] If δ is the intensity transmissivity of the gate for the FID and ε is the intensity transmissivity (leakage) of the gate for the input pulse, the total transmitted signal spectrum is given by

$$I_{\text{trans}}(\omega) = |\sqrt{\varepsilon}\,E(\omega) + i\sqrt{\delta}\,\chi(\omega)E(\omega)|^2, \tag{1}$$

$$I_{\text{trans}}(\omega) \approx \varepsilon|E(\omega)|^2 - 2\sqrt{\delta\varepsilon}\,\text{Im}[\chi(\omega)]\,|E(\omega)|^2. \tag{2}$$

The signal-to-background ratio will now be

$$S/B = 2\sqrt{\delta/\varepsilon}\,|\text{Im}\,\chi(\omega)|\,. \tag{3}$$

Therefore the expected increase in detection sensitivity will be $\sqrt{\delta/\varepsilon}$, the square root of the on-to-off intensity-grating-efficiency ratio. So, to realize a tenfold enhancement in sensitivity, one must gate out 100 times more of the input pulse energy than the FID. Figure 2 shows the effect of time gating the transmitted light on the spectrum of the signal for a sample with two absorption lines within the pulse spectrum. The increased sensitivity comes at the expense of total signal strength, but this is typically not a problem in linear absorption measurements.

In practice, the gate must have a fast rise time and a slow fall time compared with the T_2 of the medium, which is ~100 ps for most atmospheric-pressure gas-phase species. Electro-optic gates have rise times that are too slow. A gate that does satisfy these requirements is diffraction from a laser-induced grating in a resonant condensed-phase medium. We have used both organic dyes and sharp-cut absorbing-glass filters, for which both population and thermal gratings can easily be formed with diffraction efficiencies greater than 0.1%. The dephasing times of these gating media are typically much shorter than those of the gas samples of interest, so they contribute only fast gate-generated (i.e., broadband) FID to the signal and so will not interfere with narrow-band absorption dips.

Figure 3 shows our gating apparatus involving 200-fs-long pulses from a frequency-doubled regeneratively amplified Ti:sapphire system. We used a phase-matched boxcars geometry.[9] Pulses 1 and 2, the gates, crossed in the gating material to form a grating. Pulse 3, the probe, passed through the sample (picking up FID) and then diffracted off the grating into the 270-mm spectrometer. We set the delay of the probe relative to the gate pulses such that the unabsorbed probe pulse passed through just before the gate formed. In this way, significantly more of the FID than the probe pulse itself diffracted into the spectrometer. A cooled CCD camera detected the diffracted signal.

To demonstrate this technique we first used an uncoated 250-μm-thick fused-silica etalon as a sample to simulate an absorbing medium with equally spaced spectral features separated by ~0.24 nm. The etalon's transmission dips were ~10% because of its reflectivity R of 3.5%. Figure 4 shows our FASTGAS experimental results. The fringe modulation has

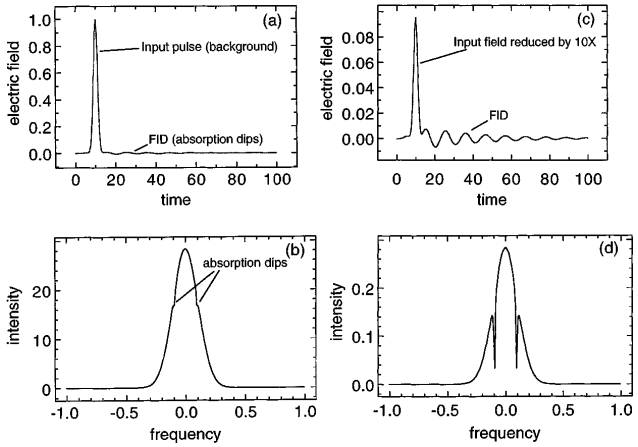

Fig. 2. Ungated pulse and (a) FID and (b) spectrum, and gated pulse and (c) FID and (d) spectrum for the case of two absorption lines. Note the change in scale for the gated FID and spectrum [(c) and (d)].

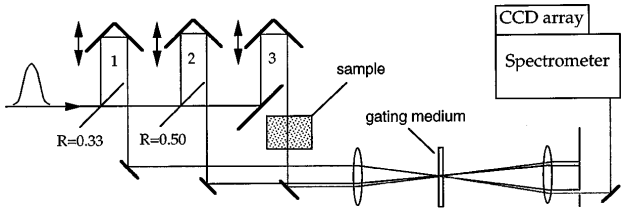

Fig. 3. FASTGAS experimental apparatus for time gating with laser-induced gratings.

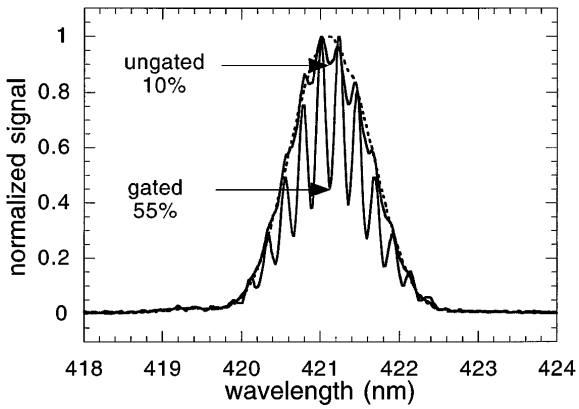

Fig. 4. Transmitted spectra for a sample consisting of an etalon. Dashed curve, input spectrum; solid curves, gated and ungated spectra. The transmission dips are enhanced by a factor of 5.5 by the FASTGAS technique.

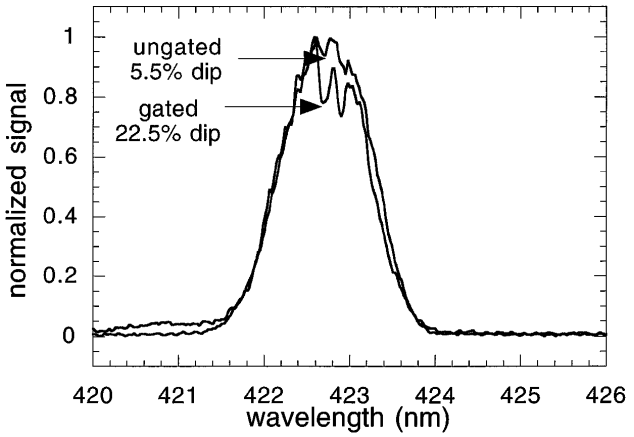

Fig. 5. Same as Fig. 4, except that a cell of NO_2 is used as the sample. The absorption dips are enhanced by a factor of 4.

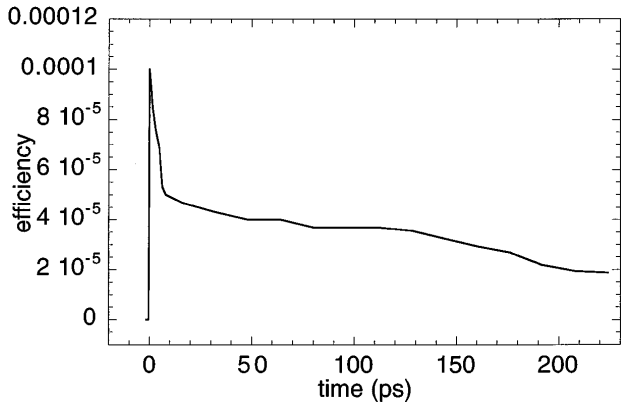

Fig. 6. Measured gate efficiency versus time for the GG420 colored glass filter.

increased from ~10% to ~55%, implying an attenuation of the unreflected input by ~30× relative to the FID. Modulation can now be observed in the gated spectrum that was not easily detectable in the ungated spectrum, i.e., in the wings of the spectrum.

We have also demonstrated FASTGAS in a 10-cm-long cell of NO_2 gas at a pressure of 5 Torr. The corresponding spectra (ungated and gated) are shown in Fig. 5. Here the sensitivity enhancement is a factor of ~4.

What factors limit the enhancement? The first is spectral resolution. When spectrometer resolution is sufficient to resolve the spectral features in the gated signal, absorption dips close to 100% should be obtainable. However, when the spectrometer cannot resolve the absorption dips, averaging with adjacent pixels reduces the dip strength and hence the sensitivity enhancement. Gating out more of the input does not compensate for such insufficient resolution. As a result, spectral resolution limits sensitivity in this technique, just as it does in conventional absorption spectroscopy. However, the relative enhancement in sensitivity is the important feature of this technique and, with increased spectral resolution, significantly larger enhancements should be achievable.

Another factor is the temporal form of the gate. The ideal step-function shown in Fig. 1 is not obtainable in practice. We obtained the measured diffraction efficiency versus time of the laser-induced grating for the colored filter glass (GG 420) by scanning the probe (in the absence of a sample) in time, as shown in Fig. 6. The lifetime of the gate (100–200 ps) is not a limiting factor unless gigahertz resolution is required and is also available in the spectrometer. In addition, the fast, nonresonant component of the filter response near zero delay is not significantly stronger than the delayed response and therefore has only a small effect on the ultimate resolution and accuracy of the technique. Also, the laser-pulse shape can be important. Satellite pulses or wings can allow extra amounts of the input pulse to reach the detector and reduce the sensitivity enhancement. None of these problems is serious, and future research will address them.

In conclusion, we have demonstrated an all-optical method for enhancing the sensitivity of single-shot broadband absorption spectroscopy. The technique (FASTGAS) relies on the use of an ultrashort input pulse that temporally separates the absorption information from the background in the transmitted signal and, in addition, on ultrafast optical gating, which suppresses the background with respect to the absorption signal.

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

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