Observation of a cw Dark-Field Signal in an Absorption Spectroscopic Experiment Using a Phase Locked Free-Electron Laser

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We introduce a technique for ultrasensitive absorption spectroscopy using the GHz-rate pulse train from a phase-locked free-electron laser (FEL), in which the fractional power absorbed from one or more laser lines reappears as a signal on the dark background between the pulses emerging from the sample. Preliminary absorption experiments in 15 Torr cm of methane at 3.25 μm, using phase-locked pulses from the Mark III FEL, clearly reveal an interpulse beat signal due to absorption by adjacent molecular rotational lines which is generated only in the presence of interpulse phase coherence.

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Contemporary remote sensing and process-control applications rely heavily on laser absorption spectroscopy for the trace-level analysis of molecular species [1], and high-resolution absorption techniques are presently capable of achieving quantum-limited sensitivities [2]. One of the most sensitive methods uses frequency modulation (FM) of a cw laser beam to probe the sample: If the wavelength is tuned so that one of the sidebands overlaps the absorption line of interest, then the differential absorption between the sidebands induces an amplitude modulation that can be detected in real time [3,4]. Recent modifications of the FM technique, in which a high-finesse Fabry-Perot cavity enclosing the sample was used to enhance the available power for absorption and simultaneously filter the laser-frequency noise, have demonstrated a noise-equivalent absorption sensitivity of 5×10^{-13} [5]. With presently achievable high-finesse optical cavities, incident milliwatt-level optical powers can yield intracavity powers of several hundred watts.

While such sensitivities are appropriate for the study of a select set of extremely weak overtone and forbidden transitions, they are difficult to achieve in measurements lying outside the tuning range of conventional lasers. In particular, the mid-IR absorption spectra of many molecular species, which would otherwise provide unique fingerprints for trace analysis, populate spectral regions for which available cw sources lack both the power and tunability to achieve comparable sensitivities over sufficiently broad bands.

In this Letter, we describe a new technique for ultrasensitive absorption spectroscopy, and we report the results of a preliminary experiment to demonstrate an essential component of that technique, i.e., the observation of a cw dark-field signal in an absorption experiment in methane using a phase-locked free-electron laser (FEL) [6–8]. "FEL modulation spectroscopy" exploits the high power and wide tunability of the FEL and is inherently capable, in principle, of both single-mode spectral resolution and quantum-limited sensitivity. The technique relies on the intrinsic modulation of the laser beam due to the mode locking effect of discrete electron bunches from an rf linac, and also on the interpulse optical phase coherence induced by a suitable interferometric resonator [9,10]. The modulation is characterized both by the multimode optical spectrum with GHz line separation and by the absence, unique to the FEL gain medium, of any optical emission, spontaneous or otherwise, in the space between the electron bunches. The technique is illustrated in Fig. 1(a), which shows the optical pulse train passing through a weakly absorbing sample. If the wavelength is tuned so that one of the laser lines overlaps the absorption line of interest, then the incident and transmitted spectra will differ only by a small, single mode component at the absorbed frequency. The difference between the input and output pulse trains will be the Fourier transform of this small, single mode component, corresponding to the presence in the interpulse regions of a weak, cw "dark signal" that can be detected in real time. The quantitative effects on such a coherent optical pulse train passing through a weakly absorbing ensemble of discrete absorbers can be deduced from the convolution of the amplitude $E_{\mathrm{inc}}(t)$ of the incident optical field with the impulse response of the

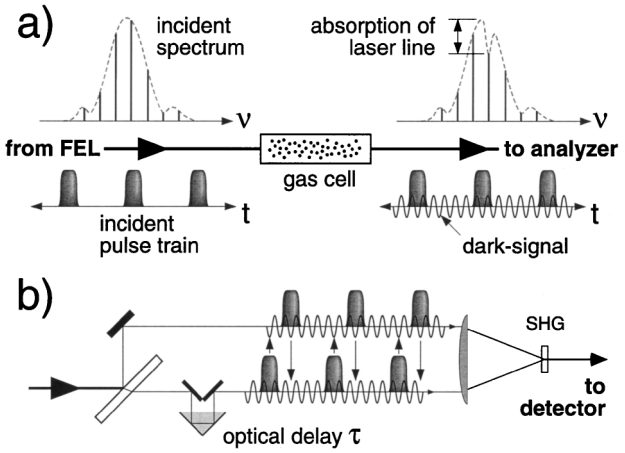

FIG. 1. FEL modulation spectroscopy; (a) dark-signal generation; (b) dark-signal detection.

elementary atomic or molecular oscillators:

$$E_{\text{trans}}(t) = E_{\text{inc}}(t) - \int_{-\infty}^{\infty} d\tau\, E_{\text{inc}}(t - \tau) \sum_{i=1}^{N} T_i(\tau),$$

where the transfer function for the ith oscillator is given by

$$\tilde{T}_i(\omega) = \delta_i \Big/ \left[1 + j\left(\frac{\omega}{\Delta\omega}\right)_i \left(1 - \frac{\omega_i^2}{\omega^2}\right)\right]$$

and δ_i, $(\Delta\omega/\omega)_i$, and ω_i are, respectively, the fractional absorption, fractional linewidth, and resonant frequency of the ith elementary oscillator.

A related technique for enhanced absorption spectroscopy has been independently proposed and recently demonstrated using broadband, coherent excitation of an absorbing medium by a single femtosecond optical pulse [11]. The pulse induces a delta function excitation of the molecular susceptibility, and the "impulse response" encoding the absorption spectrum trails behind the pulse as free-induction decay. A conventional laser generally will not be free of spontaneous emission in the region surrounding the pulse, however, and the spectral resolution of the single-pulse technique is limited by the spectrometer apparatus, in contrast to the single-mode resolution provided by the GHz pulse repetition rate in FEL modulation spectroscopy.

The FEL detection method and apparatus are illustrated in Fig. 1(b). The transmitted pulses from the sample are sent through a crossed-beam autocorrelator designed to measure the intensity autocorrelation function using second-harmonic generation (SHG). If the optical delay is adjusted so that the pulses in the two paths are interleaved, then any dark signal present between the pulses will be converted into second-harmonic light with an efficiency determined by the megawatt power of the copropagating pulses. The method thus provides both spectral (SHG) and geometric (crossed-beam) isolation of the dark signal. In the configuration of Fig. 1(b), the dark detection is symmetric about the optical pulses; single-sided detection would be realized by placing the sample within one arm of the autocorrelator. Self-conversion of the megawatt pulses in each beam, which can scatter into the detector at small crossed-beam angles, can be effectively reduced by using orthogonally polarized beams with an appropriately oriented nonlinear crystal [12]. In such a geometry the megawatt pulses experience negligible depletion, and on time scales greater than their picosecond duration they act as delta functions that extract the true time dependence of the dark signal. A nonuniform time dependence would be revealed if several laser lines were absorbed by the sample; the dark signal would then exhibit beats.

Because of the direct detection of the signal against a dark background, the signal-to-noise ratio (SNR) in FEL modulation spectroscopy differs fundamentally from the quantum limit of FM spectroscopy. Specifically, while quantum shot noise in FM spectroscopy is generated by the full intensity I of the pump laser irradiating the detector, the quantum shot noise in FEL modulation spectroscopy is generated only by the frequency-doubled dark signal, which is reduced from the incident intensity I of the absorbed line by the fractional absorption κ and the conversion efficiency $\eta(I)$. If N_e, β, and N_L, respectively, scale the contributions of electronic noise, shot noise, and laser fluctuations to the SNR, then FM spectroscopy exhibits an SNR given by [4]

$$\text{SNR}_{(\text{FM})} = \frac{\kappa I}{\sqrt{N_e^2 + (\beta\sqrt{I})^2 + (N_L I)^2}} \rightarrow \kappa \frac{\sqrt{I}}{\beta},$$

where the arrow indicates the quantum limit. In FEL modulation spectroscopy, the corresponding SNR is

$$\text{SNR}_{(\text{FEL})} = \frac{\eta\kappa I}{\sqrt{N_e^2 + (\beta\sqrt{\eta\kappa I})^2 + (N_L \eta\kappa I)^2}} \rightarrow \sqrt{\eta\kappa}\, \frac{\sqrt{I}}{\beta}.$$

Since κ can be on the order of 10^{-13} in some experiments, and $\eta(I)$ is typically on the order of 10^{-2}, the sensitivity of FEL modulation spectroscopy can, in principle, exceed the sensitivity of FM spectroscopy by 6 orders of magnitude. The achievable sensitivity is enhanced in any event by the optical powers of the incident laser lines from the phase-locked FEL, which can individually exceed several hundred watts on microsecond time scales [13].

We have performed absorption experiments in methane gas at 3.25 μm using the Mark III FEL [14], both to confirm the generation and detection of dark signal and to demonstrate its dependence on interpulse optical phase coherence. The Mark III FEL is mode locked by a 2.86 GHz train of picosecond electron bunches from a 40 MeV rf linac and delivers a 2.86 GHz output train of transform-limited, picosecond optical pulses with energies of several microjoules. The pulse trains are cycled in "macropulses" with durations of several microseconds. Since the rf frequency is 39 times the 73.3 MHz round-trip frequency of the optical resonator, the resonator contains 39 circulating optical pulses which, in the absence of an interpulse coupling mechanism, build up independently from noise with random relative phases. To induce interpulse phase coherence, adjacent pulses are coupled by an intracavity Michelson interferometer [15], and the resulting coherence is characterized in the frequency domain by an axial mode separation of 2.86 GHz. In contrast, the line spacing in the non-phase-locked laser is 73.3 MHz, with 39 axial modes in each 2.86 GHz rf band, each mode oscillating with a random spectral phase.

In the present experiments, the Michelson beam splitter was one surface of a CaF_2 plate at 71° incidence with a P-polarized reflectance of 5.5%. The theoretical mode reduction for this interferometer was confirmed by spectral measurements at 3 μm. Output coupling was provided by the second surface but was misaligned from the beam splitter leakage in the far field by a wedge angle ground into the plate. The resonator was similar to previous experiments on the Mark III FEL [16] except for the CaF_2 beam splitter,

which had the advantage in the present experiments of facilitating laser oscillation even when the interferometer was detuned, thus allowing us to readily eliminate and reestablish the phase coherence of the pulse train. Detuning the interferometer on the scale of the picosecond pulse duration (by $\sim$600 μm, or 4 ps round-trip in the present experiments) did have the effect of inducing a delay of less than a microsecond in the laser turn-on time due to increased reflection losses from the beam splitter surface.

In the laser configuration established in the experiment, the optical pulses had a duration of 1.1 ps and a spectral width of $\sim$30 cm^{-1} at 3.25 μm. The methane spectrum at this wavelength is dominated by R-branch rotational lines separated by 9.4 cm^{-1}, with linewidths ranging from 0.1 to 0.3 cm^{-1} due to a Coriolis fine structure in the excited vibrational state [17]. The picosecond laser spectrum therefore overlapped roughly three of these rotational lines, each of which enveloped between one and three rf bands of the laser spectrum ($\Delta\nu_{\mathrm{rf}} = 2.86$ GHz $= 0.095$ cm^{-1}). Consequently, even in the phase-locked mode of operation, a single laser axial mode could not be isolated for selective absorption as depicted in Fig. 1. Instead, by altering the axial mode spectrum through phase locking, we could exploit the presence of adjacent rf bands within each rotational line to excite either coherent or incoherent absorption by the overlapping fine structure components. Doppler linewidths were calculated to be 280 MHz, and homogeneous linewidths were estimated to be $\sim$5 MHz at the 1.5-Torr pressure used in the experiment [18].

The laser beam was delivered to the methane cell and autocorrelator through a 30-m vacuum transport line held below 1-mTorr pressure, and a path length of 2.6 m in air. The copropagating laser harmonics were blocked with a 3-mm-thick Ge plate, and the 3.25-μm fundamental beam was passed once through the 103-mm-long gas cell. The autocorrelator used an orthogonally polarized, crossed-beam design with an antireflection-coated, type-II phase matched $AgGaS_2$ crystal and a Ge photodiode detector.

Autocorrelation scans using the phase-locked and non-phase-locked laser beams, taken in succession both with and without the gas cell, are shown in Fig. 2. The phase-locked laser macropulse was 2 μs long with an output energy of 9 mJ, yielding an attenuated peak power of 500 kW at the gas cell. The scans display the transient signal just after turn-on of the laser, with amplification chosen to reveal the weak features on the wings. The scans without the gas cell [Figs. 2(a) and 2(b)] show only noise outside of the main pulse, as expected for the FEL, except for satellite peaks at a delay of 10–15 ps. These peaks cannot be attributed to multiple reflections in the apparatus; the observation that they are shifted by the Michelson detuning between the phase-locked and non-phase-locked cases indicates that they originated in the laser, most likely from spontaneous emission by low energy electrons which may have leaked around the momentum filter in the electron gun.

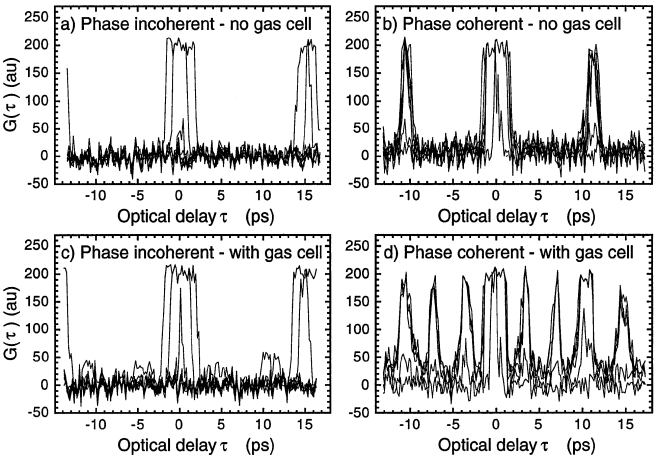

FIG. 2. Measured autocorrelation function $G(\tau)$ after turn-on of the laser macropulse, for the configurations labeled. The amplifier was saturated by the main laser pulse at zero delay.

In the measurements using the gas cell, the scan with the non-phase-locked laser [Fig. 2(c)] is mainly devoid of dark signal except for evidence of weak absorption at delays of 5 and 11 ps. The absence of dark signal is consistent with destructive interference of the randomly phased axial modes spanning multiple Doppler-broadened lines. In contrast, coherent excitation by the phase-locked laser [Fig. 2(d)] yields a deeply modulated dark signal with a 3.6 ps period corresponding to the 9.4 cm^{-1} rotational line spacing in methane. In either case, the nearest multiple reflection from the 2-mm-thick CaF_2 windows on the gas cell would appear at a delay of 19 ps. The fractional absorption was calculated from the published data for methane to be 1.5% for each rotational line [19], or $\sim$150 mW per line for the incident spectral powers used in Fig. 2(d), and 2×10^{-4} for the entire spectral energy in the pulse train. These levels of absorption were smaller than the laser fluctuations.

The temporal evolution of the dark signal is illustrated in Fig. 3, which displays the full macropulse records from

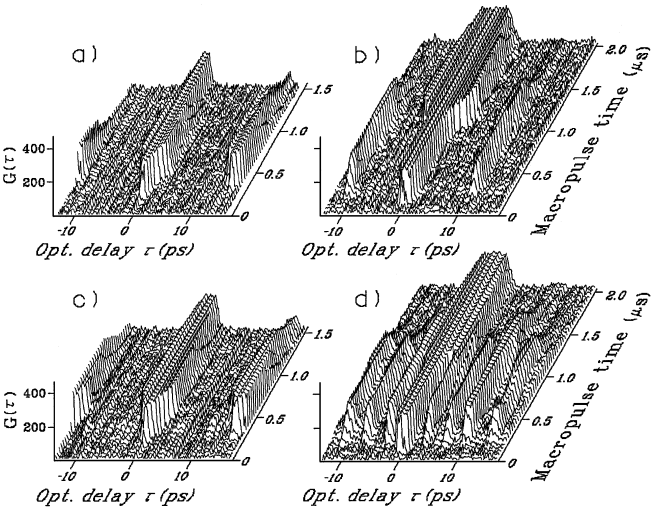

FIG. 3. Evolution of the autocorrelation function $G(\tau)$ during the macropulse, for the respective traces in Fig. 2.

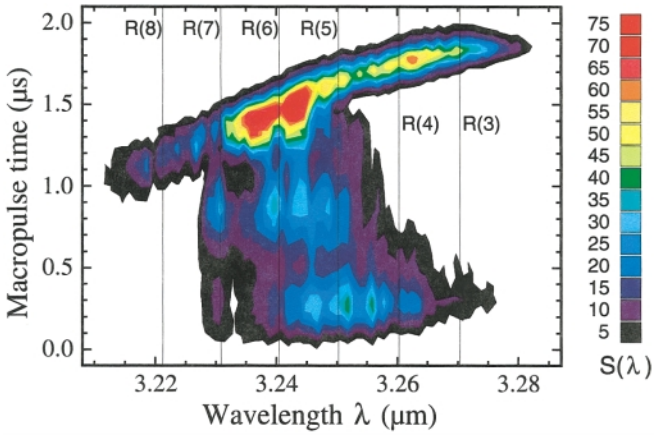

FIG. 4 (color). Evolution of the laser spectrum $S(\lambda)$ during the macropulse, with locations of the methane rotational lines $R(3-8)$. Laser power (arb. units) is encoded in color.

Fig. 2. The dark signal induced by the methane absorption persists for at least 1 μs. However, all of the secondary peaks decay before the end of the main laser pulse, ruling out their possible origin as multiple reflections in the apparatus. No mechanism can account for a loss of phase locking, which depends only on the cold cavity mode structure [15]. However, the loss of signal is correlated with the evolution of the laser spectrum shown in Fig. 4, which displays a rapid slew of the laser wavelength, at a rate of 0.07 μm/μs, beginning about 1 μs into the laser macropulse (this frequency sweep was due to the droop in electron energy at the end of the pulse caused by increased beam loading, pulse-forming-network ripple, and modulation of the rf drive power applied to the high power klystron; this modulation also appears to have suppressed the leakage of the low energy electrons past the momentum filter in the gun). The disappearance of the dark signal is attributable to the rapidity of the frequency sweep, since appreciable absorption is possible only over intervals longer than the inverse homogeneous linewidth of 200 ns. These time domain observations demonstrate the efficacy of the dark-signal technique to distinguish fundamental line broadening mechanisms, while the persistence of the dark signal over microsecond intervals is consistent with the capability of the technique to achieve sub-MHz resolution.

We are continuing to develop the theory and technique of FEL modulation spectroscopy for real-time applications in trace-gas analysis, process control, and remote sensing, including the use of aperiodic and multiply periodic input pulse trains to deconvolve the effects of inhomogeneous and homogeneous broadening. In addition to improving the spectral resolution and detection sensitivity, methods to increase the laser mode spacing and spectral purity will facilitate the selection and identification of absorption features within complex spectral backgrounds. We are constructing an interferometrically stabilized, Fox-Smith laser resonator capable of tunable, high power, single-mode outputs [20], and have procured a tunable Fabry-Perot etalon to externally increase the mode spacing by harmonic filtering of the pulse train. A preferred technique to increase the mode spacing is to harmonically mode lock the laser with a nonintegral number of intracavity pulses. When combined with phase locking in high gain systems, this technique would increase the laser mode spacing and brightness at the source while preserving the dark background between the pulses, which we have already demonstrated to be critical for the interpretation of results.

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