Infrared spectroscopy is of basic importance for the characterization of materials in many fundamental and applied sciences. For example, infrared spectra can quantify chemical composition in the chemical industry or reveal the mechanisms of conductivity of semiconductors and superconductors. The widely used Fourier-transform infrared spectrometer (FTIR) commonly relies on an incoherent thermal source that emits a multioctave spectrum to cover at least the 3–30-μm wavelength region where so-called fingerprint vibrational absorption permits chemical identification. The incoherent spreading of a thermal infrared beam, however, reduces the potential application of FTIR microscopy and also limits long-distance environmental probing. Coherent infrared sources can overcome this limitation. Of these sources, gas and semiconductor lasers have the drawback of limited tuning capability, whereas free-electron lasers require a large support facility. Only rectified ultrashort light pulses have been shown to be highly suitable to produce purely time-domain interferograms that encode the infrared spectrum. The advantages of this spectrometer compared with the common FTIR include ease of operation (no moving parts), speed of acquisition (100 μs demonstrated), and not-yet-shown collimated long-distance propagation, diffraction-limited microscopic probing, and electronically controllable chemometric factoring. Extending time-domain frequency-comb spectroscopy to lower (terahertz) or higher (visible, ultraviolet) frequencies should be feasible. © 2004 Optical Society of America

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Infrared spectroscopy can be done in a purely time-domain manner, rendering obsolete the cumbersome mechanical delay methods that have been limiting the performance of both incoherent FTIRs and coherent THz infrared spectrometry.

Both FTIRs and THz spectrometers handle the task of massively parallel spectroscopic probing by interferometric detection. Our spectrometer retains the principle of combining two interferometer beams but differs in how these beams are generated in the first place. Instead of splitting a common input, we use two inputs from two independent sources. Thus we can offset their frequencies to facilitate multifrequency heterodyne signal processing. To understand our concept in a frequency picture, consider a coherent frequency-comb beam that contains a harmonic series of evenly spaced frequencies $nf_r$, where $n = 1 \ldots N$. The superposition of a second coherent frequency-comb beam with slightly different frequency spacing $f'_r = f_r - \Delta$, where $\Delta < f_r/2N$, then forms a “coherent dual beam,” which exhibits, by interference, unique power modulation at $nf_r - n(f'_r - \Delta) = n\Delta$. Each modulation element $n\Delta$ can be viewed as a heterodyne signal that uniquely measures one comb component. All modulations together can be viewed as a time-domain interferogram that, when it is Fourier transformed into the frequency domain, results in a harmonic radio-frequency comb spectrum $n\Delta$ that is an exact replica of the dual beam’s spectrum. The optical system of a coherent frequency-comb spectrometer thus consists of a coherent dual beam, a sample, and a detector. We demonstrated this concept earlier with a microwave spectrometer. In that spectrometer, a coherent dual beam that covered the 0.01–1-THz range was generated purely electronically, by independent frequency multiplication (up to $N \approx 300$) of two continuous monochromatic microwaves at nearly identical frequencies that had been generated by two synthesizers.

Basic to the time-domain coherent FTIR reported here is the highly stable repetition frequency $f_r$ that is obtainable with mode-locked lasers and the accordingly precise, equidistant comb of emitted optical frequencies. Our setup (Fig. 1) uses two independent, mode-locked Ti:sapphire (Ti:S) lasers. They emit trains of 20- and 12-fs pulses, respectively, at near-visible wavelengths at ∼800 nm, with repetition rates $f_r \approx 87$ MHz with a difference of $\Delta = 2$ Hz. It is well known that the frequency combs emitted by such lasers are generally not harmonic; rather, each frequency $nf_r$ in a given comb is offset by a common offset frequency $f_0$. We use both beams to generate mid-infrared radiation by focusing the beams separately onto 0.5- and 1-mm-thick GaSe crystals (Fig. 1). Second-order nonlinearity generates difference frequencies $nf_r + f_0 - mf_r - f_0 = (n - m)f_r$, and
characteristic minimum occurs at known filter functions. From these observations the spectra and to allow us to compare the changes with the detector to monitor changes induced in the radio high-pass type were placed in the beam path before alignment. Imperfections in this preliminary setup, both in the base. Minima in the spectrum indicate etaloning FTIR, as will the linearity of the acquisition time spectral resolution of a time-domain frequency-comb

\[ n(f_r - \Delta) + f_0' - m(f_r - \Delta) - f_0' = (n - m)(f_r - \Delta), \]

which not only lie in the mid-infrared but, most importantly, constitute harmonic combs because the offsets cancel exactly. We collimate both mid-infrared beams and superimpose them onto a ZnSe combiner to form the desired mid-infrared coherent dual beam. In monitoring the power with a HgCdTe mid-infrared detector we readily observed the anticipated characteristic power modulations [Fig. 2(a)], which are mid-infrared interferograms. They appeared about twice a second, when the pulses of the two lasers coincided. Note that these interferograms arise from a purely time-domain scanning with no moving parts, in contrast to known FTIRs and THz spectrometers.

Fourier transforming the interferogram in Fig. 2(a) reveals the radio spectrum in Fig. 2(b), which represents the mid-infrared spectrum at the impressive frequency downscaling by the nominal factor \( f_r / \Delta = 43.500.000 \). This is a nominal value only, because the difference \( \Delta \) in repetition frequencies of the two free-running Ti:S lasers is not exactly 2 Hz but fluctuates and drifts by \( \sim 1 \) Hz during several minutes. Consecutively recorded spectra exhibit a similar shape but at slightly varied frequency scaling [as is evident from the example in Fig. 2(c)]. This variation is caused by a slow fluctuation or drift of \( \Delta \) on a \(<1\) s time scale. The similarity of consecutive spectra is evidence, however, that the frequencies (and amplitudes) of both infrared harmonic combs remain highly stable on the short time scale that is needed for acquiring a single interferogram (100 \( \mu \)s). Thus an intermediate feedback-loop bandwidth of \( \sim 1 \) kHz applied to stabilize \( \Delta \) in a future setup could well eliminate the frequency-scaling fluctuations; this would facilitate averaging over many consecutive interferograms to improve the signal-to-noise ratio, as is accepted practice with common FTIRs. The degree of stabilization of \( \Delta \) that is achievable will limit the spectral resolution of a time-domain frequency-comb FTIR, as will the linearity of the acquisition time base. Minima in the spectrum indicate etaloning imperfections in this preliminary setup, both in the GaSe phase matching and in the beam combiner alignment.

Infrared filters of the low-pass, bandpass, and high-pass type were placed in the beam path before the detector to monitor changes induced in the radio spectra and to allow us to compare the changes with known filter functions. From these observations the characteristic minimum occurs at \( \sim 1000 \) cm\(^{-1} \), an assignment that is also compatible with the known sensitivity function of the detector that rises from 10% at 720 cm\(^{-1} \) to 90% at 800 cm\(^{-1} \). For further display we correct the spectra that we obtained for detector roll-off of \( \sim f^{-2} \) and normalize them to have the minimum at 1000 cm\(^{-1} \) and to reach unity at the second maximum. The results [Fig. 3(a)] again show that the infrared spectra attained in this preliminary demonstration of time-domain coherent FTIRs have a reproducible shape. The frequency scale could in principle be precisely calibrated by gas-phase molecular absorption lines. As a preliminary step in this direction we applied trichloroethylene gas, which evaporated rather uncontrollably, from an open plastic beaker, with some drops of liquid trichloroethylene placed below the beam near the detector. This gas is known to exhibit several mid-infrared absorption bands of \( \sim 20\) cm\(^{-1} \) width at atmospheric pressure, the strongest centered at 850 and 940 cm\(^{-1} \). Figure 3(b) shows that the spectra obtained are indeed modified by the gas. The most prominent dip extends from 930 to 960 cm\(^{-1} \) and thus supports the frequency scale that we adopted.

Our experiment verifies our novel concept of using precision lasers to transport broad optical–infrared spectra into the electronic realm. The demonstrated

![Fig. 1. Optical system of a coherent FTIR. Two femtosecond lasers with slightly different pulse repetition frequencies generate, by rectification in GaSe, two infrared beams that are superimposed onto a ZnSe combiner. No mechanically moving part is involved.](image1)

![Fig. 2. (a) Infrared interferogram recorded by the HgCdTe detector. (b) Infrared spectrum calculated by Fourier transformation. (c) Infrared spectrum from a subsequent recording; the slightly changed frequency scaling is due to laser drift.](image2)

![Fig. 3. Four consecutive spectra superimposed and normalized as described in the text: (a) without and (b) with infrared-absorbing vapor in the beam path before the detector.](image3)
mid-infrared spectrum spans nearly an octave, from 750 to 1300 cm\(^{-1}\). It could be extended beyond 2000 cm\(^{-1}\) up to the near visible by use of thinner crystals\(^7\) and certainly down to the far infrared, THz, and microwave regions by use of suitable crystals, antennas, combiners, power detectors, and sampling methods. Better alignment and summing interferograms will boost the signal and allow much longer interferograms to be recorded for increased spectral resolution.

As is well known, length \(L\) of an interferogram directly determines the maximally possible spectral resolution as \(1/L\). In common FTIRs the length \(L\) stands for the optical path-length difference attained, such that \(1/L\) is the resolution limit given directly in units of inverse centimeters, independently of wavelength. In our time-domain frequency-comb FTIR the radio interferogram is recorded for a time \(T\), so the spectral resolution attainable is \(1/T\), which is 10 kHz for the conditions of Figs. 2 and 3. When we apply the same frequency scaling as for the spectrum of Fig. 2(b), for example, we expect 13 cm\(^{-1}\) for the attainable mid-infrared spectral resolution. Interestingly, the resolution element \(\delta f > 13\) cm\(^{-1}\) that we can achieve at present integrates coherent amplitude and phase contributions of as many as \(\delta n > 4500\) adjacent infrared comb frequencies. Clearly, extending acquisition time \(T\) from the current 100 \(\mu s\) to 1.5 ms could improve the spectral resolution limit to 1 cm\(^{-1}\), which is a value often used in conventional FTIRs. This of course would require that the Ti:sapphire lasers remain stable during this longer time. Ultraprecision methods of laser stabilization are already known\(^4\) that not only would be sufficient for even single infrared comb modes to be resolved but furthermore would permit electronic fine tuning of their frequencies.\(^7\) Further, it appears that a coherent dual beam is an appropriate means to obtain broadband Fourier-transform spectroscopy also in the near-infrared, visible, and ultraviolet spectral ranges. If that Fourier transform were based on Ti:sapphire lasers, stabilization of offset frequencies \(f_0\) and \(f_0'\) would be required,\(^5\) which would give the interesting, unique advantage that by choice of \(f_0 \neq f_0'\) the radio spectrum \(n\Delta\) could be conveniently transposed and compressed to the range \(f_0 - f_0' + n\Delta\).

Reaching far beyond conventional FTIRs, coherent frequency-comb FTIRs promise microsecond acquisition for the study of fast, single event dynamics, e.g., in polymers and biopolymers. The coherent FTIR’s laserlike beam permits long-distance probing for remote environmental analysis as well as diffraction-limited focusing for microscopy. Other sample configurations, for instance, total internal reflection for high-sensitivity biomolecular screening and photoconduction for semiconductor and superconductor research, are feasible. The unused second output beam from the combiner (Fig. 1) can contribute on-line reference interferograms. Finally, the sample can be placed before the combiner to produce a complex-valued FTIR—with simultaneous amplitude and phase infrared spectra—thus enabling complex optical constants to be determined in reflection without recourse to ellipsometry and also facilitating complex-valued scattering-type near-field microscopy\(^10\) for nanometer-resolution chemical analysis of nanocomposites.

The method of time-domain coherent infrared spectroscopy can also be used for narrowband spectroscopic and metrologic applications. In these applications the procedure of recording an interferogram with subsequent Fourier transformation would be replaced by other means of electronic processing. For example, lock-in amplification of the detector signal could permit continuous monitoring of the amplitude and the phase of a single radio-frequency component \(n\Delta\), which represents a single infrared frequency \(nf_r\). Note that one could rapidly switch the monitored infrared frequency, simply by switching the lock-in amplifier’s reference. Generally, a factoring approach to integrating weighted contributions from different infrared bands that characterize a given material could be conveniently made by purely electronic means and thus would establish a versatile method for performing on-line infrared chemometrics.

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