

Fast, real-time spectrometer based on a pulsed quantum-cascade laser

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We describe a mid-infrared spectrometer that is based on the combination of a multiple-pass absorption cell and a submicrosecond pulsed quantum-cascade laser. The spectrometer is capable of both making sensitive measurements and providing a real-time display of the spectral fingerprint of molecular vapors. For a cell with a path length of 9.6 m, dilution measurements made of the ν_9 band transitions of 1,1-difluoroethylene indicate a sensitivity of 500 parts in 10^9 , corresponding to a fractional absorbance of 4×10^{-4} . © 2003 Optical Society of America

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Recent advances in the fabrication of pulsed quantum-cascade (QC) lasers have permitted the achievement of devices that work at or close to room temperature while they produce pulses with peak powers that are in excess of 1 W with duty cycles approaching 100%. The operating wavelength associated with QC lasers fall typically in the 3–15- μm window and so makes the QC laser an ideal light source for probing the spectral features associated with the fundamental rotational and vibrational absorption bands of gaseous molecules, as was discussed in a recent review paper by Kosterev and Tittel.¹

Most spectrometers based on pulsed QC lasers^{2,3} use a short-duration current pulse applied to the QC laser. This current generates a pulse in the spectral domain, which is then tuned through the absorption feature of interest by use of a slowly varying subthreshold current ramp. The resultant frequency tuning is a quadratic function of the applied current for which a correction must be made.^{2,3} With this technique, spectral scans of 0.23 cm^{-1} (Ref. 2) to 0.74 cm^{-1} (Ref. 3) have been achieved. To achieve trace-level sensitivity one applies a modulation of several kilohertz to the current ramp to permit phase-sensitive detection, limiting the rate at which data are collected. Another severe restriction arises from the fact that the applied current pulse defines the effective linewidth of the emitted radiation, restricting the spectral resolution of the spectrometer. Namjou *et al.*² showed that, when a 10-ns-duration current pulse was applied to their QC laser, the effective linewidth was 0.023 cm^{-1} .

Our approach to measuring the spectral fingerprint of a given molecular gas differs significantly from the previous approach^{2,3} in that we rely on the linear frequency downchirp that is induced when a top-hat current pulse is applied to a QC laser to scan the oscillating frequency through the transitions of interest. It was shown previously⁴ that the extent of the frequency window that is covered depends on the duration of the applied current pulse. The fact that there is a linear correlation between the temporal and the spectral profiles means that we can record the temporal profile of a generated pulse and use

the result to infer the spectral nature of the pulse. Thus we can observe and record the spectral profiles of molecular gases in real time at high repetition rates, which will facilitate the rapid collection and the subsequent averaging of these data, thereby bringing about improvements in the signal-to-noise ratio. The resolution of our spectrometer is limited not by the effective linewidth but by the temporal resolution of the detection system. As a result, our spectrometer opens the potential for simultaneous measurement and identification of several molecular gases, such as short-lived chemical intermediates.

The experimental arrangement of our spectrometer was as follows: The output from a distributed-feedback QC laser was collected and collimated by an off-axis parabolic mirror–germanium telescope arrangement to produce a beam of 3-mm diameter, which was subsequently passed into a White cell. The mirrors in this cell were separated by 0.6 m and configured to give 16 passes, corresponding to an effective path length of 9.6 m. After traversing the White cell the light was then focused onto a high-speed mercury cadmium telluride detector. The output from this detector was then amplified and coupled to a digital oscilloscope. The temporal resolution of the detection system was estimated to be 2 ns, limited by the 500-MHz bandwidth of the oscilloscope.

The QC laser was mounted upon a Peltier cooler, which allowed the temperature to be varied from -40°C to $+40^\circ\text{C}$, and was housed in an air-tight chamber. The temperature of the substrate was stabilized to a level of $\pm 0.01^\circ\text{C}$. The laser oscillated at a wavelength of $10.26 \mu\text{m}$ (974 cm^{-1}) at 0°C . The radiation was coupled from this chamber via an antireflection-coated ZnSe window. The QC laser was excited electrically by an in-house designed power supply that generated pulses with durations that ranged from 3 to 200 ns at repetition rates of as much as 8.3 MHz with peak currents as great as 20 A. Previous measurements made with this laser⁴ indicated that the oscillating wave number can be temperature tuned at a rate of $-7.6 \times 10^{-2} \text{ cm}^{-1}/\text{K}$. Furthermore, we have shown that the rate of change

of wave number with respect to pulse duration is $-6.1 \times 10^{-3} \text{ cm}^{-1}/\text{ns}$. This downshift is independent of the temperature of the QC laser substrate but depends on the current applied to the laser.⁵ More importantly, for a constant-amplitude pulse current and a submicrosecond pulse duration the frequency downchirp is linear across this window. Figure 1 shows the temporal and the spectral profiles of a typical pulse emitted by our QC laser. The spectral profile was measured by use of a Fourier-transform spectrometer (FTS) with a resolution limit of 0.0015 cm^{-1} . By comparing the spectrum of 1,1-difluoroethylene when the gas was probed by use of a blackbody emitter as the light source and the spectrum when the QC laser was used as the light source for the FTS it was possible to obtain an estimate of the QC laser linewidth (see Fig. 2). To understand how an estimate of the laser linewidth can be obtained it is necessary to consider the way in which the effective instantaneous linewidth of the source affects the recording of the spectrum. The spectrum recorded with a pulsed QC laser may be regarded as the wave-number domain equivalent of the spectra recorded by Sharpe *et al.*⁶ They produced a wave-number swept pulse by applying a current sweep to a narrowband continuously operating, cryogenically cooled QC laser and recorded the spectra in the time domain with a high-speed detector. They have shown that the linewidth of the absorption lines, recorded as a function of time, may be understood as the convolution of the Gaussian width associated with the Doppler broadening and a laser line width, both of which are calculated in the wave-number domain.

In comparing the two spectral profiles of 1,1-difluoroethylene, as shown in Fig. 2, we replaced the fast detector used by Sharpe *et al.*⁶ with a spectrometer with high resolution in the wave-number domain. The spectrum that this instrument records should therefore correspond to that calculated by Sharpe *et al.*, which is a convolution of the Doppler-broadened linewidth and the laser linewidth. The final linewidth recorded by the FTS would then be the convolution of the Doppler and the laser linewidths, which is then itself convolved with the instrumental line shape of the FTS. Because the total effective linewidth recorded in this way appears to be no greater than that which results for the spectral resolution of the FTS, the linewidth of the instantaneous laser linewidth will have an upper limit of 0.0015 cm^{-1} (45 MHz).

In recording the data shown in Fig. 2 we sampled $\sim 7 \times 10^7$ pulses; any significant temporal or amplitude pulse fluctuations would have caused a smearing of the recorded profile. Hence we believe that the pulse train is highly reproducible. With this rapidly scanning, reproducible, and narrow-linewidth light source we should be able to make a direct measurement of the absorption bands of any molecular gas that absorbs within the wave-number region covered by our QC laser without having to step tune the QC laser through the absorption band.

To demonstrate the effectiveness of our proposed spectrometer we set the substrate temperature of

the laser to be 273 K; the laser was driven with a pulse of 200-ns duration with 4.6-A amplitude, corresponding to a rate of change of wave number of $-7.1 \times 10^{-3} \text{ cm}^{-1}/\text{ns}$. The resultant spectral output from the laser covered a wave-number window of $973.0\text{--}974.4 \text{ cm}^{-1}$, again determined by the use of the FTS as described in Ref. 4. The White cell was filled

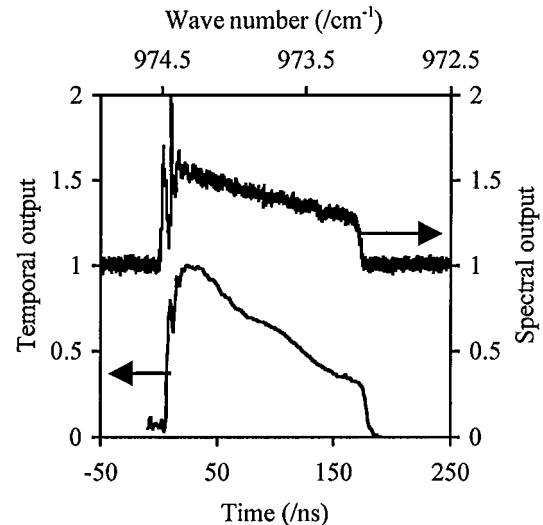


Fig. 1. Typical temporal and spectral profiles of a pulse emitted by the QC laser.

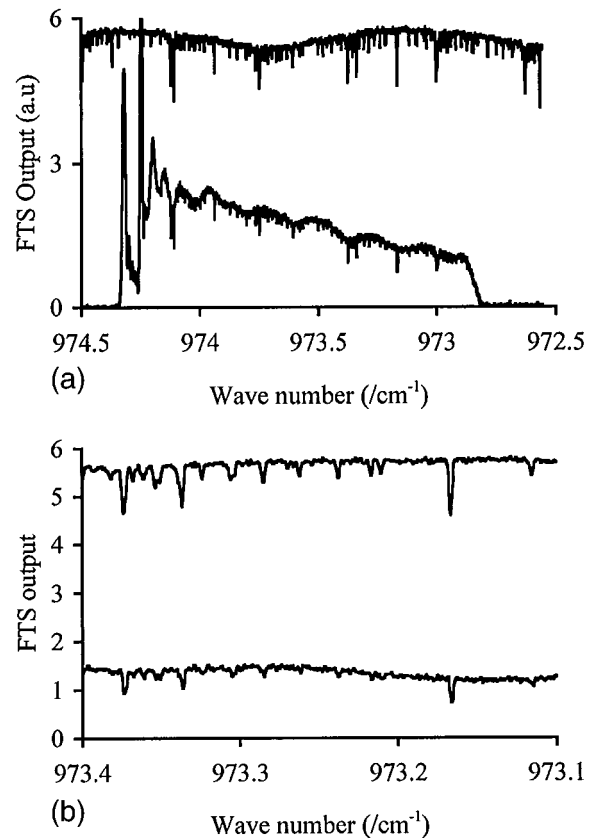


Fig. 2. (a) Comparison of the spectrum of 1,1-difluoroethylene as measured by use of FTS when either a blackbody (top trace) or a QC laser (bottom trace) acts as the light source. (b) Expanded view of the traces shown in (a).

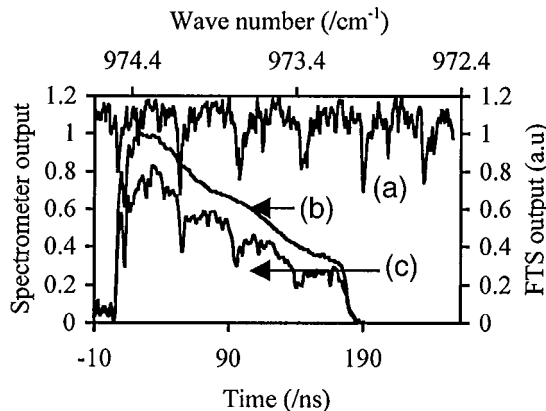


Fig. 3. Output from the spectrometer (b) when no 1,1-difluoroethylene is present and (c) when 1,1-difluoroethylene is present. (a) Reference transmission spectrum of 1,1-difluoroethylene.

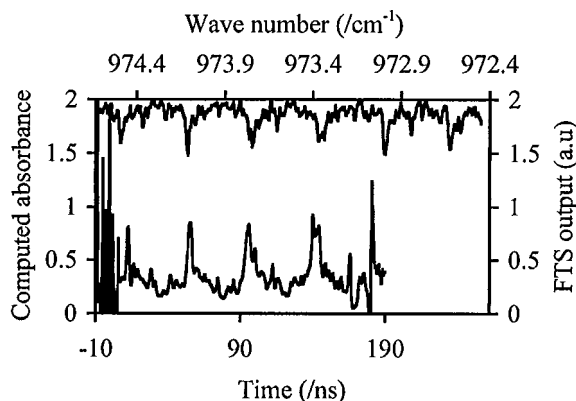


Fig. 4. Bottom, computed absorbance profile together with top, a reference transmission spectrum of 1,1-difluoroethylene.

with 1,1-difluoroethylene to a pressure of 0.75 Torr, and the signal transmitted through the White cell was displayed in real time on the oscilloscope and is shown in trace (c) of Fig. 3. In this mode of operation the spectral resolution of our spectrometer was limited by the temporal resolution of our detection system, which is 2 ns, corresponding to a spectral resolution of 0.013 cm^{-1} , which is significantly less than the 0.023 cm^{-1} reported by Namjou *et al.*² To determine whether the output from the spectrometer was a faithful representation of the spectrum associated with the gas we compared the signal with that recorded by a FTS [trace (a) of Fig. 3]. Comparison of these two spectra indicates that there is a strong correlation between the two signals. We further verified this correlation by comparing the computed absorbance with the FTS spectrum as shown in Fig. 4. The origin of the structure at the start of the computed absorbance signal (lower trace of Fig. 4) is as follows: We evaluated the absorbance by taking the natural logarithm of the ratio of the transmission

through the spectrometer with no gas present to the transmission with gas present. Pulse-to-pulse fluctuations in the baseline before the arrival of each pulse significantly affect this ratio, which resulted in the observed structure.

To determine the sensitivity of our spectrometer we performed a simple dilution experiment in which the spectrum of the gas was recorded while the concentration of the gas was reduced. For the gas under investigation we were able to determine the sensitivity to be 500 parts in 10^9 , corresponding to a fractional absorbance of 4×10^{-4} . This value compares well with that observed by other research groups that have used QC laser based spectrometers to study molecules such as N_2O and CH_4 . For example, Kosterev *et al.*³ observed a minimal detectable absorbance of 3×10^{-4} when they measured the spectrum associated with N_2O .

In conclusion, we have demonstrated a simple real-time mid-infrared spectrometer that is capable of making sensitive measurements of the concentration of molecular vapors as well as providing a display of the molecular fingerprint associated with that gas. We have shown, for the first time to our knowledge, that it is possible to make direct measurements of the chemical fingerprint associated with a heavy molecular gas. We are currently identifying those factors that limit both the spectral resolution and the sensitivity of our system and intend to report on them subsequently. We believe that our system has the potential to operate in many kinds of environment and, with the recent advances in quantum-cascade laser technology, provide sensitivities greater than can be measured as parts in 10^9 .

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