Cavity ringdown spectroscopy using mid-infrared quantum-cascade lasers

B. A. Paldus and C. C. Harb

Informed Diagnostics, Inc., Suite I, 1050 Duane Avenue, Sunnyvale, California 94086-2626

T. G. Spence and R. N. Zare

Department of Chemistry, Stanford University, Stanford, California 94305-5080

C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, and A. Y. Cho

Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974

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Cavity ringdown spectra of ammonia at 10 parts in 10^9 by volume (ppbv) and higher concentrations were recorded by use of a 16-mW continuous-wave quantum-casacde distributed-feedback laser at 8.5 μm whose wavelength was continuously temperature tuned over 15 nm. A sensitivity (noise-equivalent absorbance) of 3.4×10^{-9} cm^{-1} Hz$^{-1/2}$ was achieved for ammonia in nitrogen at standard temperature and pressure, which corresponds to a detection limit of 0.25 ppbv. © 2000 Optical Society of America

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Cavity ringdown spectroscopy (CRDS), based on detecting the rate of decay of light exiting a high-finesse optical resonator, is becoming a convenient means of trace-gas analysis.[1] CRDS systems have evolved from pulsed laser sources coupled into linear resonators to more-complex cavity-locked systems employing ring resonators and stabilization circuitry.[1] Lasers ranging from the ultraviolet to the mid infrared have already been used for CRDS. The true potential of CRDS for ultrahigh-sensitivity trace-gas detection will remain limited, however, until inexpensive, practical sources in the mid infrared become available. Such sources would make it possible to use this technique to detect the fundamental vibrational transitions of molecular species, that is, the so-called infrared molecular fingerprint region.

The advent of and continuous improvement in the performance of quantum-cascade distributed-feedback (QC-DFB) semiconductor laser technology may provide an almost ideal source for CRDS in the mid infrared. Quantum-cascade lasers are based on electronic transitions between quantized conduction band states of a multi-quantum-well structure.[2] These bands are designed through band-structure engineering and grown by molecular beam epitaxy.[3] By design, quantum-cascade lasers are capable of emitting at mid- and long-infrared wavelengths (3–17 μm).[2] QC-DFB lasers can be tuned continuously up to 50 nm, emitting tens to hundreds of milliwatts,[4] and have linewidths of the order of megahertz when they are unstabilized and of tens of kilohertz when they are stabilized.[5] QC-DFB lasers can be operated either in pulsed mode at room temperature or in continuous mode (cw) at cryogenic temperatures. To date, QC-DFB lasers have been employed in wavelength-modulation spectroscopy[6] [5×10^{-5} noise-equivalent absorbance (NEA)], cw mode rapid-scan direct absorbance spectroscopy[7] (3×10^{-6} NEA), and photoacoustic spectroscopy[8] (8×10^{-6} NEA). In this Letter we report on the application of a cw QC-DFB laser at 8.5 μm to CRDS of ammonia.

The QC-DFB laser was mounted inside a liquid-helium-cooled cryostat that was described in Ref. 8. The cryostat's single-mode output was continuously tuned over 15 nm by sweeping of the laser heat-sink temperature from 35 to 60 K. A home-built, low-noise current driver was employed to operate the laser. The far-field beam profile of a QC-DFB laser is near Gaussian,[9] so the laser can easily be matched to a transverse mode of a high-finesse optical resonator.

The polarization was measured with a half-wave plate and a 500:1 polarizer consisting of a series of germanium plates at Brewster's angle. QC-DFB lasers were found to be linearly polarized perpendicular to the laser growth plane, with a ratio of 60:1. These polarization characteristics are sufficient to permit the use of polarization-dependent ring resonators for CRDS.

Figure 1 presents the experimental setup, which is the unlocked equivalent of ring-resonator CRDS systems reported previously.[10] The cavity round-trip length was 42 cm (714-MHz free spectral range), and the mirror reflectivity was 99.95% for p-polarized light

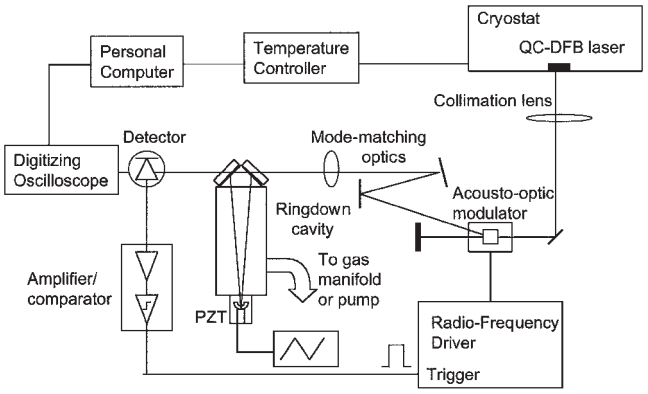

Fig. 1. Block diagram of the CDRS.[9] PZT, piezoelectric transducer.

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and 99.97% for *s*-polarized light. Over the 15-nm wavelength scan of the laser, the mirror reflectivity changed by 50 parts in 10^6 from its nominal value at 8.490 μm. The frequency shift between *p*- and *s*-polarized light was measured to be 300 MHz.

Mode matching of the QC-DFB laser to the ringdown cavity produced primarily TEM_{00} mode excitation. Higher-order transverse ringdown cavity modes accounted for at most 30% of the total coupling. Figure 2 shows the transmission through the optical resonator as the resonator length is changed in time. The smallest measured linewidth was 4 MHz over a 500-μs period, which includes the unstabilized laser linewidth, the unstabilized *p*-polarization cavity linewidth (120 kHz), and relative instabilities between the laser and the cavity.

At first, the system, which was filled with nitrogen, was characterized at a fixed laser heat-sink temperature (fixed wavelength). Then ammonia was added to the nitrogen and the laser source was swept in frequency by temperature tuning. Ringdown signals were acquired in a manner similar to that reported by Romanini *et al.*[11] In this procedure the optical resonator is swept through a free spectral range, which ensures that radiation will build up in the cavity. When sufficient buildup is achieved, an acousto-optic modulator is triggered, and radiation is no longer deflected into the optical resonator. The ringdown rate can then be measured. This scheme allows ringdown waveforms to be acquired without the need to lock together the laser and the cavity.

As the laser frequency was slowly tuned (3 nm/min), the ringdown cavity was swept back and forth through a free spectral range with a frequency of 300 Hz. The ringdown decays were detected with a HgCdTe detector (50-MHz bandwidth). These operating conditions allow data to be acquired at an effective repetition rate of 600 Hz by use of a Gagescope 8012 12-bit analog–digital digitizing card. The acquisition speed was limited to 600 Hz by data transfer to the computer. The ringdown cavity can be swept at a rate of up to 8 kHz, allowing potential data-acquisition rates of 16 kHz. The ringdown decay for *p*-polarized light was used because its superior cavity transmission produced a signal-to-noise ratio that was limited by the digitization process.[10] The *p*-polarization decay constant was 0.939 μs.

Figure 3 presents the statistics of the measured cavity decay time (shot-to-shot statistics) for ~500 consecutive sweeps of the cavity for the asynchronous, unstabilized cw CRDS system. In recording these data, we either filled the ringdown cavity with an atmosphere of nitrogen (Praxair, Medipure grade) or evacuated it to 0.1 Torr. Both conditions produced similar shot-to-shot statistics. The laser was at a constant temperature (wavelength). The normalized shot-to-shot standard deviation of the measured cavity ringdown decay ($\sigma_{\Delta\tau/\tau}$) was 2×10^{-3} for a collection of approximately 500 scans, corresponding to an absorbance single-shot standard deviation (σ_α) of 8.3×10^{-6} cm^{-1}. The estimated single-shot residual (i.e., the difference between the measured and the HITRAN96[12] spectra) converted to absorption is 7.3×10^{-8} cm^{-1}, corresponding to a NEA of 3×10^{-6}. By averaging of 600 shots, the single-shot standard deviation was reduced to 10^{-4} (the limit of the digitizer) and the sensitivity of the measurement became 4.2×10^{-9} cm^{-1}/Hz$^{-1/2}$. This value corresponds to a NEA of 1.7×10^{-7}.

The actual measured single-shot spectral residual was 8.3×10^{-8} cm^{-1}, 14% higher than the stationary statistical data. Figure 4(a) illustrates a single-shot scan obtained with 5 parts in 10^6 of ammonia, compared with the spectrum generated from the HITRAN96 database for standard temperature and pressure. Note that the laser mode hopping observed in previous photoacoustic spectroscopy experiments[8] was not present, which is most likely the result of using optics having a superior antireflection coating.

Averaged spectra (600 scans) were obtained at various concentrations of ammonia. The smallest

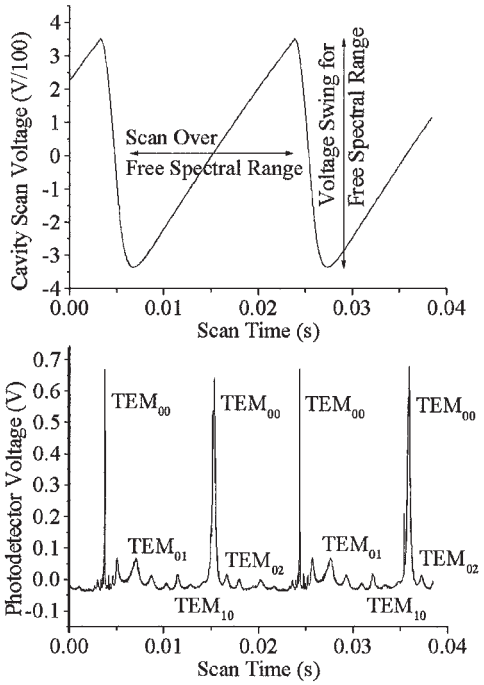

Fig. 2. Optical resonator transmission (bottom) as a function of frequency when the cavity length is swept in time, with a voltage sweep (top).

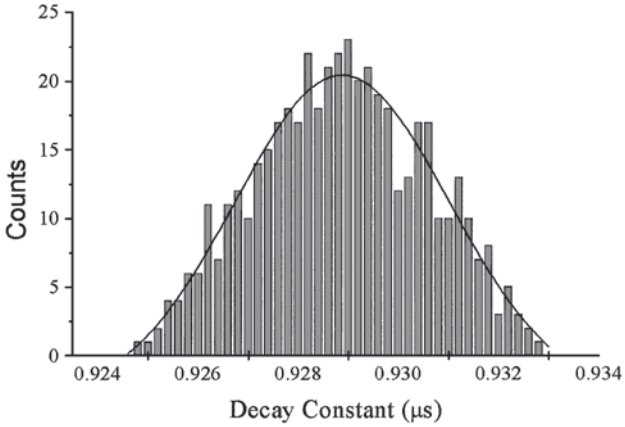

Fig. 3. Single-shot statistics for 500 shots, for a stationary wavelength ($\lambda = 8.45$ μm at $T = 45.3$ K) and a ringdown cavity filled with nitrogen.

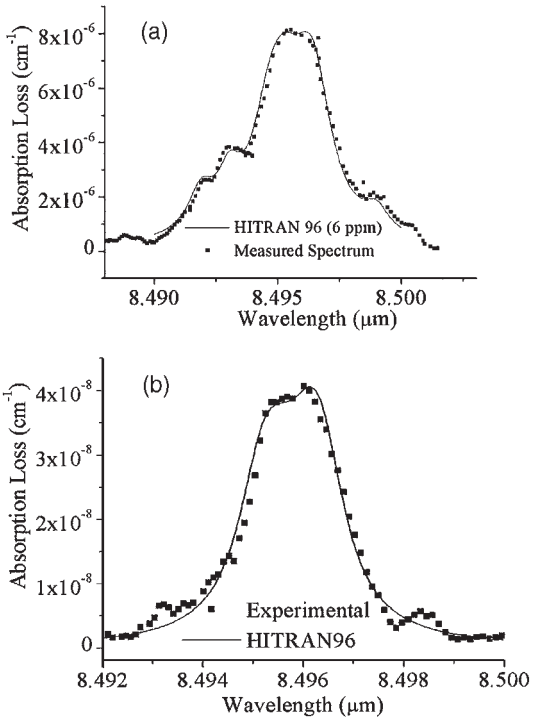

Fig. 4. (a) Single-shot spectrum of 4-ppmv ammonia in nitrogen compared with a spectrum generated by HITRAN96. (b) Averaged spectra of 10-ppbv ammonia at STP.

concentration achievable with the mixing manifold was ~100 parts in 10^9 by volume (ppbv) of ammonia in nitrogen. The total absorption loss was directly proportional to the ammonia concentration. Therefore we could estimate smaller concentrations of ammonia from a semipurged system based on the absolute optical loss measured inside the ringdown cavity. The smallest concentration, shown in Fig. 4(b), corresponds to 10-ppbv ammonia and was obtained by direct dilution of the cavity sample with additional nitrogen. The signal-to-noise ratio of this spectrum corresponds to a detection limit of 0.25 ppbv.

By using the integrated absorption line shape rather than the peak absorption, it is possible to improve the system's detection limit significantly.[13] For single-shot scans the minimum detectable absorbance limit for the integrated line shape was 1.8×10^{-8} cm^{-1}. For averaged measurements (600-Hz repetition rate), the measured minimum detectable absorbance limit was 1.0×10^{-9} cm^{-1}.

The sensitivity reported here is less than the minimum detectable absorbance limit of 1.0×10^{-12} cm^{-1} that was recently achieved in the near infrared by use of specially designed analog electronics[12] but represents an improvement in CRDS sensitivity for mid-infrared systems.[14] The sensitivity could have been improved by construction of a ringdown cavity with a longer ringdown lifetime. Nevertheless, the results are comparable to those obtained with a cavity-locked diode laser system, owing to the higher repetition rates for data collection. The unstabilized QC-DFB laser was almost as stable in frequency as the near-infrared external-cavity diode laser used previously.[10] Because the absorption strength of the ammonia feature is significantly stronger than that of the water overtone reported previously,[10] the overall detection limit in the mid infrared is 3 orders of magnitude better.

This preliminary performance of QC-DFB laser CRDS in the mid infrared therefore lends credence to the belief that electronically locking the QC-DFB laser and the ringdown cavity may yield extreme detection sensitivities in the near future. As QC-DFB lasers become routinely available, we can look forward to their increasing use in cavity ringdown spectroscopy for practical applications.

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