Rapid, wide bandwidth pulsed cavity ringdown spectroscopy

Toby K. Boyson,[1] Dylan R. Rittman,[2] Thomas G. Spence,[3]
Maria E. Calzada,[3] Abhijit G. Kallapur,[1] Ian R. Petersen,[1]
K. Paul Kirkbride,[4] David S. Moore,[2] Charles C. Harb[1*]

[1] School of Engineering and Information Technology, UNSW Canberra,
Canberra, ACT 2600, Australia
[2] Shock and Detonation Physics Group, Los Alamos National Laboratory,
Los Alamos, NM 87545, USA
[3] Department of Chemistry, Loyola University New Orleans,
New Orleans, LA 70118, USA
[4] Forensic and Data Centres, Australian Federal Police, Weston, ACT 2611, Australia

*To whom correspondence should be addressed; E-mail: c.harb@adfa.edu.au.

Cavity ringdown spectroscopy (CRDS) is a highly sensitive direct-absorption spectroscopic technique, but one whose limitations have prevented its use for the rapid sensing of explosives. We present a new variant of the technique that is able to scan across more than 1400 nm of the mid infrared, acquiring and analysing more than 150,000 spectral datapoints in less than four seconds. We have taken spectra of acetone and nitromethane at various pressures to demonstrate the applicability of the technique to the detection of compounds with spectral features in the same region as common explosives. The wide tunabilty, rapid analysis time, and robust instrumentation of our technique would make it suitable for the rapid analysis of explosives.

An ideal explosives sensor would combine sensitivity and selectivity with a rapid analysis time; generally, however, a given instrument is designed to optimise one of these at the expense of the others. Ion mobility sensors (*1*), for example, are commonly used in airports as they are able to rapidly analyse samples, but they do not offer the sensitivity and selectivity of other techniques when the analysed sample contains unknown compounds. Dogs are probably the most commonly thought of method of detecting explosives; however, while they are efficient and portable, they are not able to unequivocally state what explosives are present, and in what concentration. Moreover, as would be expected from any animal, dogs get tired, and have at least some degree of variability in their response to stimuli amongst different animals, and even with the same animal on different occasions (*2*). The best use of dogs then is as a search tool, combined with another method to positively identify the presence and concentration of explosives. Many different techniques have been reported in the literature for the analysis of explosives (see, for example, (*3, 4*)), but all lack, in some manner, in speed, sensitivity, or selectivity.

Research has been performed on replicating some aspects of dogs and other biological systems to refine them into highly sensitive sensors that do not have the disadvantages of using an actual animal (*5*). These biologically based or inspired systems hold promise, but few are mature technologies that are ready to be brought to market. These sensors have sensitivity and selectivity, with detection limits as low as ng/mL in solution being common (*5*). The high specificity and high sensitivity of these sensors makes them attractive; however, they do not have the ability to be easily reconfigured. This high selectivity is advantageous if the explosive in question is known; it can, however, also be a disadvantage if the explosive is unknown (such as in broadscope luggage screening, or in forensic post-blast analysis). A more general spectroscopic or spectrometric method (such as mass spectrometry or absorption spectroscopy) has the ability to detect all explosives, rather than just the species that a given sensor is designed for.

Ion mobility spectrometry is commonly used in airports, and is especially useful for use by untrained operators. The gas phase mobility measurement that is intrinsic to the technique gives only a small amount of information per compound. This is acceptable for known explosives (or drugs), but limits the technique if the sample to be analysed contains unknown explosives. Mass spectrometry, either coupled to gas chromatography or liquid chromatography, is presently the technique of choice in forensic post-blast analysis, but large, expensive equipment is required and the analysis time is long due to the requirement for chromatography prior to mass spectrometry. MS does, however, offer extremely high detection sensitivities.

Spectroscopic techniques have the potential to offer the best combination of sensitivity, selectivity, and speed, and are non-destructive (unlike MS). Sensitive, indirect techniques such as laser induced fluorescence (LIF) and photoacoustic spectroscopy (PAS) have been applied to explosives detection, but they suffer from an inability to detect non-fluorescing species (for example, triacetone triperoxide (TATP)) and a sensitivity to atmospheric noise, respectively. Broadband direct absorption techniques (such as Fourier Transform infrared spectroscopy (FTIR)) offer rapid analysis times and broad spectral bandwidths, but tend to not have the spectral resolution, or be sensitive enough. Very sensitive, high resolution techniques, such as locked CRDS instruments (*6, 7*) or Noise Immune Cavity Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS) (*8*), tend to offer low spectral bandwidths, restricting their ability to distinguish absorption features of interest from interfering absorptions. Moreover, these techniques rely on complicated experimental setups that are ill suited to use outside of a laboratory. The broader the tuning range, the more information is gathered, and thus the more potential there is to discriminate explosives from innocent substances such as nitromusks present in perfumes and personal care products: this is especially relevant to large, nitro- containing species, whose spectra tend to have broad peaks, rather than the narrow, rotationally resolved peaks studied with commercial CRDS instruments.

Cavity ringdown spectroscopy is a technique that, rather than measuring relative attenuation after a light source passes through a sample, measures the temporal decay of a light field within an optical cavity. The benefits here are twofold: the cavity provides a long effective pathlength (several kilometres being common); and the measurement of a decay constant rather than intensity decouples the measurement from laser intensity noise. This means that even noisy, pulsed lasers are able to be used to acquire spectra with high sensitivity (*9*). Ramos (*10*) and Usachev (*11*) used CRDS in the UV to study vapour phase DNT and TNT: while the instrument was sensitive (due to the high absorption cross sections for the nitro group in that wavelength range), the low tunability and the broadness of spectral features in UV would make it difficult to unambiguously assign spectral features to a compound, even without the presence of masking or interfering species. The same authors (*12*) report that the UV light can cause the molecules inside the cavity to dissociate and breakdown: this would further complicate the narrow spectral bandwidth spectra. Snels (*13*) used CRDS in the near infrared (NIR), scanning across 100 nm with a centre wavelength of 1550 nm. While they report detection limits on the order of nanograms for TNT and DNT, their implementation resulted in only being able to acquire 33 ringdown events per second: this resulted in it taking tens of seconds to acquire a single spectrum, and several minutes to acquire an adequate signal-to-noise for unambiguous identification of the compound. Moreover, they only scan across a single absorption feature (due probably to the tuning range of the external cavity diode laser used in the work): this would make it challenging to unambiguously identify a given compound. The area that shows the most promise for the detection is the mid infrared (MIR): Todd *et al.* (*14*), using a pulsed optical parametric oscillator (OPO) took spectra for several common explosives from 7-8 μm. The repetition rate of their laser was 25 Hz: this limited the rate at which spectra could be acquired, with Todd noting that a practical implementation of the instrument would only monitor several wavelengths, rather than the entire spectrum. While this would increase the throughput of their technique, it would limit the ability to resolve peaks in the presence of interfering absorptions. Clearly, a better approach would be to increase the rate at which the instrument could acquire and analyse data: ideally, the technique should be limited by the scan rate of the laser, and not by the time taken to process the data.

We report here on a variant of Pulsed CRDS that is able to acquire more than 150,000 spectral datapoints in less than four seconds, while scanning across more than 1400 nm in the mid infrared. Most CRDS experiments treat the analysis of ringdown data as a time-domain problem: some method is used to build up light in the cavity, then, when the light has reached a predetermined level, the light is shuttered and the exponential decay of the cavity is measured. This decay is typically fit with a non-linear least squares fitting algorithm: this scheme is appropriate for a slow pulsed instrument, but for faster throughputs, the fitting fails to keep up with the rate of data collection (in our experience, by up to two orders of magnitude (*7, 9*)). There is, through the Fourier transform, a frequency domain approach. The cavity acts as a low pass filter (with a corner frequency of $1/\tau$ rad/sec) with respect to any modulation on the incident light:, giving an an alternative view of CRDS: rather than thinking about τ decreasing as a function of absorption within the cavity, we can think about the corner frequency of a low pass filter moving to a higher frequency as the absorption inside the cavity increases. By exciting the cavity with amplitude modulated light (in this work, a pulse train, but we have shown the technique to be applicable to squarewave modulated light as well (*7, 9, 15*)) and measuring the relative attenuation of several frequency components, τ can be calculated. For the case here, where we are using a pulse train, and measuring the ratio of the second harmonic to the fundamental, τ is given by:

$$\tau = \frac{1}{\omega}\sqrt{\frac{1-P}{4P-1}} \tag{1}$$

Where P is the magnitude of the ratio of the second harmonic to the fundamental. This methodology has several advantages over a traditional time-domain fitting algorithm: the detection bandwidth is very narrow; we are able obtain and analyse data as it arrives from the spectrometer, rather than having to acquire a ringdown and batch process; and, as we are measuring ratio of frequency components, we maintain the insensitivity to amplitude fluctuations on the incident laser light that is an important attribute of a cavity ringdown measurement. The frequency domain view of the cavity has been applied before in Cavity Attenuated Phase Shift Spectroscopy (CAPS) (*e.g.* (*16*)), where the phase shift on the modulation is measured after passing through the optical cavity: our technique has an advantage over CAPS in that we do not need to measure a reference phase at the input to the cavity. This greatly simplifies the setup and alignment procedure, as well as eliminating the need for an extra detector. A typical CRDS experiment (and essentially all of the commercially available instruments) focus on using very high reflectance (*R*) mirrors, with *R* on the order of 99.995 %, or 50 ppm. This level of *R* leads to a ringdown time of 25 μs or so, or, in the frequency domain view, a corner frequency of about 6 kHz. The use of high reflectivity mirrors increases the effective pathlength of the measurement; there is, however, a drawback to using such high Reflectors: if a ringdown transient is generated, and acquired for 5-10 times the ringdown time (i.e. 100-300 μs) and the data are fit with non-linear least squares, the throughput of the instrument is limited to less than a hundred Hz. If several ringdown events are averaged for each spectral datapoint, this slows the throughput even more. Here, we demonstrate that moderate reflectance mirrors allow a sensitive measurement without sacrificing throughput.

Here we present a spectrometer design that is simple and robust, with a view to the development of a rugged and small spectrometer. While the techniques in (*17,18*) offer excellent sensitivities and broad tuning ranges, the instruments themselves are too complicated to operate effectively outside of a research environment. A simplified diagram of the instrument is shown in Figure 1. It consists simply of a Quantum Cascade Laser (QCL) (Daylight Solutions TLS-21060, in this work set at a pulse rate of 130 kHz), an optical cavity (fitted with three $R = 99.9\%$ mirrors and one $R = 99.8\%$ mirror, giving an empty cavity ringdown time of the order of 1 μs, or, equivalently, a cavity corner frequency of 160 kHz) , detector (Kolmar KMPV8-1-J1/DC MCT), and a pair of lock-in amplifiers. The data from the lock-in amplifiers were digitised at 40 kHz, and either analysed in Labview, or exported and post-processed in Matlab. The system is simple to align and operate.

We have taken spectra of nitromethane and acetone to demonstrate the utility of our system and technique. While these species have much higher vapour pressures than most of the common explosives, their use allows us to compare absorbers of equivalent strength at a given pressure, and allows us to demonstrate that we are able to simultaneously observe spectral features from both species. We also note that the nitro peaks would be present in any nitro-containing explosive, and that the carbonyl stretch of acetone would be present in TATP as a residue. In order to gather the spectra, the cavity was purged, and then evacuated using a tur-

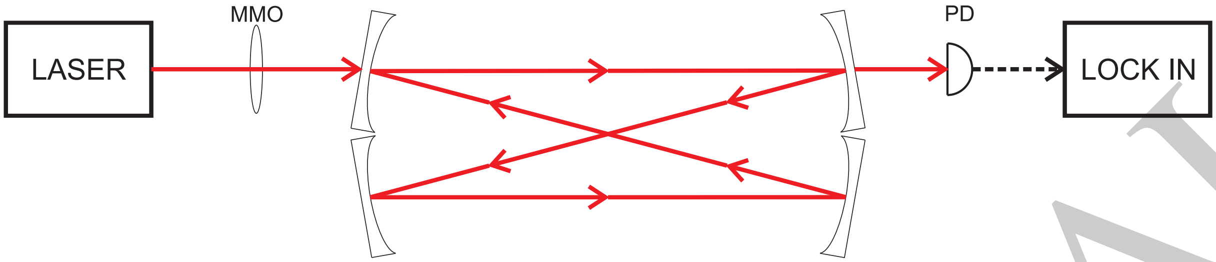

Figure 1: Schematic of the CRDS experiment. LASER is a Daylight Solutions pulsed MIR QCL (TLS-21060 with model 1001-TLC controller), tuneable from 6.2-7.6 μm, PD is a liquid nitrogen cooled mercury-cadmium-telluride photodetector (Kolmar KMPV8-1-J1/DC MCT), LOCK IN are a pair of lock-in amplifiers, configured to measure the in phase and quadrature components of the fundamental and the second harmonic of the pulse train after it passes through the cavity. Optical paths are shown in red; electrical in dashed black. The data from the lock-in amplifiers were digitised using a National Instruments 100 kHz data acquisition card, and processed in Labview, or exported and post-processed in Matlab

bomolecular pump to $\approx 10^{-6}\ Torr$. Vapour from nitromethane, acetone, or both, was allowed into the cavity. Spectra were then acquired by sweeping the laser wavelength while acquiring the output of the lock-in amplifiers. By progressively pumping out more vapour from the cavity after each spectral run, we generated the spectra shown in Figures 2, 3, and 4. Each spectrum is generated from the average of four sweeps, each of 152,000 separate datapoints, with scan time of 3.8 seconds per sweep. The large tunability of our instrument allows us to observe both the symmetric and antisymmetric nitro stretches (Figure 3, 7.3 μm and 6.3 μm respectively) as well as two strong methyl stretches of acetone (Figure 2, 7.4 μm and 6.9 μm). The advantage of this large bandwidth is demonstrated in Figure 4: despite the symmetric nitro stretch from nitromethane being swamped by the strong acetone absorbance, we are still able to resolve the antisymmetric stretch.

In order to quantify the noise equivalent absorbance of our instrument and technique, we have used the methodology of Zalicki and Zare (*20*). The minimum detectable absorption loss (MDAL) is expressed in terms of the minimum detectable loss per cm or optical path length with a hypothetical one second of averaging time (*i.e.*, units of $cm^{-1}/\sqrt{Hz}$). The best result

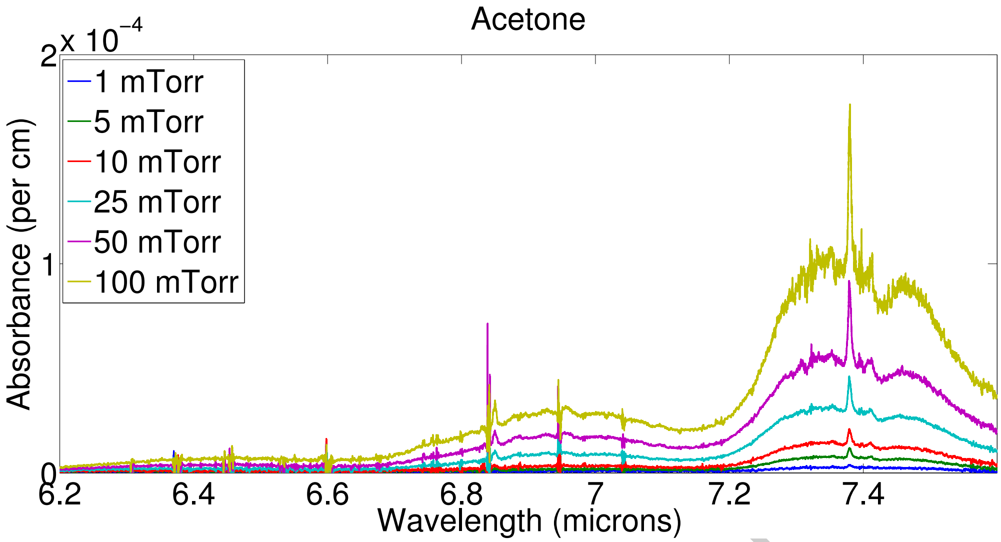

Figure 2: Experimental acetone spectra at varying pressures

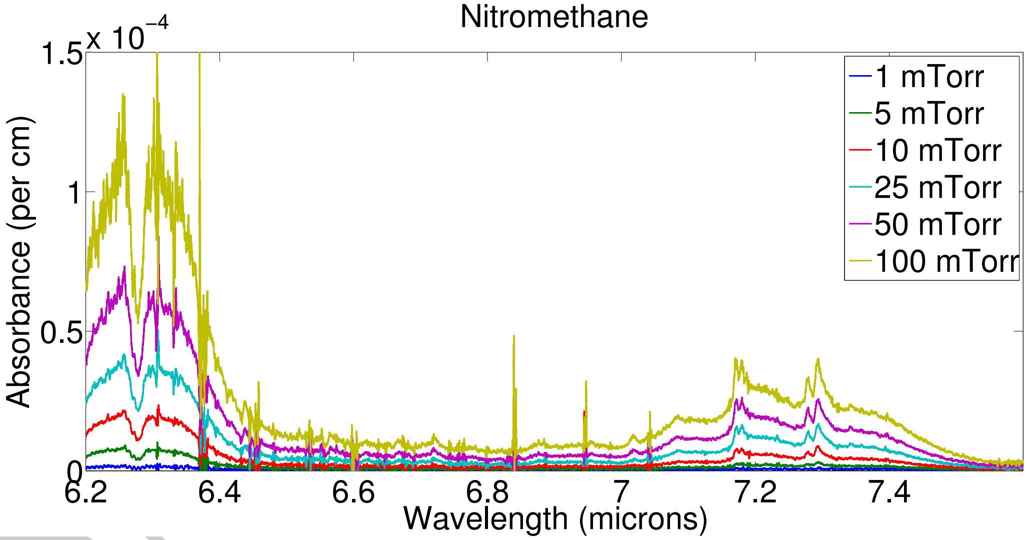

Figure 3: Experimental nitromethane spectra at varying pressures

for a CRDS experiment, $\approx 10^{-12}\ cm^{-1}/\sqrt{Hz}$ was published by Spence *et al.* (*6*), but this was a complicated experiment that was only able to scan across several nanometers. More typical pulsed CRDS experiments achieve MDALs of the order of $\approx 10^{-9}\ cm^{-1}/\sqrt{Hz}$. The MDAL is

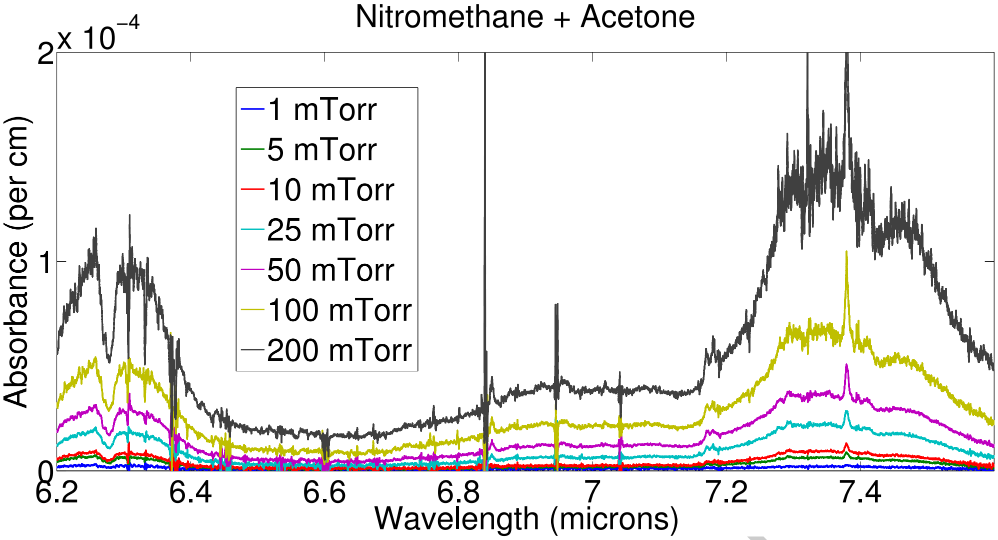

Figure 4: Experimental spectra for a mixture of acetone and nitromethane at varying pressures

calculated from:

$$MDAL_{raw} = \frac{1}{c}\left(\frac{1}{\tau - \Delta\tau} - \frac{1}{\tau}\right) \tag{2}$$

where $\Delta\tau$ is some measure of the standard deviation for a given measurement set (here, it is the 2σ deviation), c is the speed of light (in cm/s). $MDAL_{raw}$ is in units of cm^{-1}: this is normalised by the square root of the time taken to acquire a spectral data point to give the $MDAL$ in $cm^{-1}/\sqrt{Hz}$. To calculate the MDAL, we have generated a background spectrum, fitted it with a polynomial, and then calculated a standard deviation from the residuals (shown in Figure 5). For these data, the standard deviation is $\approx 1.2 \times 10^{-8}$ seconds. Given a mean τ of 7.8×10^{-7} seconds, and assuming a sweep time (time taken to scan across the wavelength range) of 3.8 seconds, and noting that the background is the average of 6 sweeps, this gives a MDAL of $8.1 \times 10^{-9}\ cm^{-1}/\sqrt{Hz}$.

Given these MDALs, we can calculate detection limits for acetone and nitromethane: given an absorption cross section of $\approx 3 \times 10^{-19}\ cm^2/molecule$ for acetone (*19*), we calculate the minimum detectable concentration as $1.03 \times 10^{-9}\ g/L$, corresponding to 0.95 *ppb*. For ni-

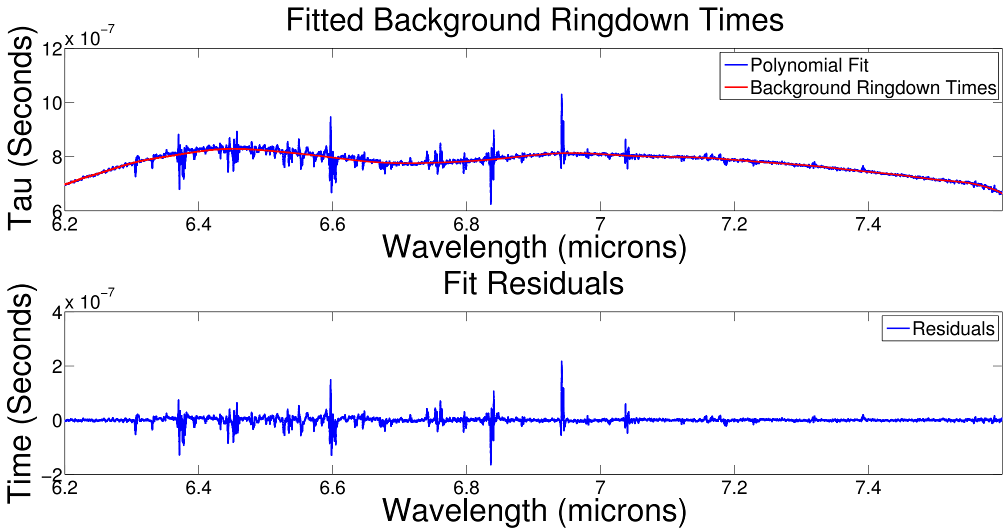

Figure 5: Fitted background spectrum for the medium finesse cavity, along with the fit residuals.

tromethane and the same minimum detectable concentration, we calculate a detection limit of 1.0 *ppb*.

We have demonstrated that cavity ringdown spectroscopy may be applied to the detection of explosives with a simple instrument that is able to rapidly scan across a large spectral bandwidth: we are able to acquire orders of magnitude more spectral datapoints than previous CRDS experiments aimed at explosives detection, and to analyse them in a fraction of the time. We are able to report noise equivalent detection limits of the order of *ppb* for acetone and nitromethane: these detection limits are gained from a very simple instrument with a very rapid analysis time. An even larger scanning range would allow for even greater selectivity: our technique allows for different lasers to be resonant in the cavity at the same time, provided that they have a different pulse frequency. We can take advantage of this to scan multiple lasers simultaneously, allowing a very large spectral bandwidth to be covered in a small amount of time. Such a system would require two lock-in amplifiers per laser, which is not viable: replacement of the lock-ins with digital signal processing (*9*) would allow for arbitrary scaling of the number of lasers, and thus the spectral bandwidth of the instrument.

References and Notes

1. R.G. Ewing, D.A. Atkinson, G.A. Eiceman, G.J. Ewing. *"A critical review of ion mobility spectrometry for the detection of explosives and explosive related compounds"* Talanta **54**(3) 515-529 (2001).

2. I.Gazit, J.Terkel. *"Explosives detection by sniffer dogs following strenuous physical activity"* Applied Animal Behaviour Science **81**(2) 149-161 (2003).

3. D.S. Moore. *"Recent Advances in Trace Explosives Detection Instrumentation"* Sensing and Imaging: An International Journal **8**, 9-38 (2007).

4. J.S. Caygill, F. Davis, S.P.J. Higson. *"Current trends in explosives detection techniques"* Talanta **88**, 14-29 (2012).

5. R.G. Smith, N. D'Souza, S. Nicklin. *"A review of biosensors and biologically-inspired systems for explosives detection"* Analyst **133**(5) 571-584 (2008).

6. T.G. Spence, C.C. Harb, B.A. Paldus, R.N. Zare, B. Wilke, R.L. Byer. *"A laser-locked cavity ring-down spectrometer employing an analog detection scheme"* Review of Scientific Instruments **71**(2), 347-353 (2000).

7. T.K. Boyson, T.G. Spence, M.E. Calzada, C.C. Harb. *"Frequency domain analysis for laser-locked cavity ringdown spectroscopy"* Optics Express **19**(9), 8092-8101 (2011).

8. J.Ye, L. Ma, J.L. Hall. *"Ultrasensitive detections in atomic and molecular physics: demonstration in molecular overtone spectroscopy"* Journal of the Optical Society of America B **15**(1) 6-15 (1998).

9. T.G. Spence, M.E. Calzada, H.M. Gardner, E. Leefe, H.B. Fontenot, L. Gilevicius, R.W. Hartsock, T.K. Boyson, C.C. Harb. *"Real-time FPGA data collection of pulsed-laser cavity ringdown signals"* Optics Express **20**(8) 8804-8814 (2012).

10. C. Ramos, P.J. Dagdigian.*"Detection of vapors of explosives and explosive-related compounds by ultraviolet cavity ringdown spectroscopy"* Applied Optics **46**(4) 620-627 (2007).

11. A.D. Usachev, T.S. Miller, J.P. Singh, F. Yueh, P. Jang, D.L. Monts. *"Optical Properties of Gaseous 2,4,6-Trinitrotoluene in the Ultraviolet Region"* Applied Spectroscopy **55**(2) 125-129 (2001).

12. C. Ramos, P.J. Dagdigian. *"Effect of photochemistry on molecular detection by cavity ringdown spectroscopy: case study of an explosive-related compound."* Applied Optics **46**(26) 6526-6532 (2007).

13. M. Snels, T. Venezi, L. Belfiore. *"Detection and identification of TNT, 2,4-DNT and 2,6-DNT by near-infrared cavity ringdown spectroscopy"* Chemical Physics Letters **489**, 134-140 (2010).

14. M.W. Todd, R.A. Provencal, T.G. Owano, B.A. Paldus, A. Kachanov, K.L. Vodopyanov, M. Hunter, S.L. Coy, J.I. Steinfeld, J.T. Arnold. *"Application of mid-infrared cavity-ringdown spectroscopy to trace explosives vapour detection using a broadly tunable optical parametric oscillator"* Applied Physics B **75** 367-376 (2002).

15. C.C. Harb, T.K. Boyson, A.G. Kallapur, I.R. Petersen, M.E. Calzada, T.G. Spence, K.P. Kirkbride, D.S. Moore. *"Pulsed quantum cascade laser-based CRDS substance detection: real-time detection of TNT"* Optics Express **20**(14) 15489-15502 (2012).

16. R. Grilli, L. Ciaffoni, A.J. Orr-Ewing. *"Phase-shift cavity ring-down spectroscopy using mid-IR light from a difference frequency generation PPLN waveguide."* Optics Letters **35**(9), 1383-1385 (2010).

17. M.J. Thorpe, K.D. Moll, R.J. Jones, B. Safdi, J. Ye. *"Broadband cavity ringdown spectroscopy for sensitive and rapid molecular detection"* Science **311**(5767) 1595-1599 (2006).

18. B. Bernhardt, A. Ozawa, P. Jacquet, M. Jacquey, Y. Kobayashi, T. Udem, R. Holzwarth, G. Guelachvili, T.W. Haensch, N. Picque. *"Cavity-enhanced dual-comb spectroscopy."* Nature Photonics **4**(1) 55-57 (2009).

19. J.J. Harrison, N Humpage, N.D.C. Allena, A.M. Waterfall, P.F. Bernath, J.J. Remedios. *"Mid-infrared absorption cross sections for acetone (propanone)"* Journal of Quantitative Spectroscopy and Radiative Transfer **112**(3), 457-464 (2011).

20. P. Zalicki, R.N. Zare. *"Cavity ring-down spectroscopy for quantitative absorption measurements"* Journal of Chemical Physics **102**, 2708 (1995).