R2-C.3: Chaotic Cavity Gas Cell for Optical Trace Explosives Detection

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II. PROJECT DESCRIPTION

Core funding for this project ends in Year 3 per the outcome of the Biennial Review process. Currently funded students will be supported via the ALERT Science and Engineering Workforce Development Program (SEWDP) (formerly known as the ALERT Career Development Grant Program) so as to not impact their degrees. Results of the student work will be reported in a special section of the ALERT Year 4 Annual Report.

A. Project Overview

This project aimed to develop compact cavities for mid-infrared (MIR) optical absorption trace gas sensing that support long optical path lengths (OPLs) and optical focusing. The research advances the overall ALERT research program by modeling, designing and characterizing, rotationally asymmetric cavities (RACs) and pairing these cavities with quantum cascade lasers (QCLs) for MIR trace explosives detection. The societal benefits include the development of technologies for MIR sensors that can be deployed in areas not currently accessible due to cost, space and personnel limitations, and the training of graduate and undergraduate students in technologies relevant to the homeland security enterprise (HSE).

The cavity plays a pivotal role in the performance, size, and cost of a sensor incorporating a multipass cell. Cavities with long OPLs are favorable because the light interacts with the gas under test over a longer effective distance, increasing the amount of absorbed light. Sensors based on optical absorption benefit from the longer OPL because the change in the intensity of the optical source is more easily measured. The RACs investigated in this project support stable, long OPLs (>5m) by engineering rotational asymmetries in the cavity shape. Another favorable aspect of the RACs in this research is that a beam can be engineered to focus as the light is reflected inside the cavity. This so-called “global focusing time” (GFT) is similar to the focusing by a lens or mirror and can be engineered via the cavity design. The ability to control the GFT is beneficial because it results in small beam spots on the surface of the cavity, enabling continuous wave operation of the optical source and a reduction in the size of the cavity.

This project also sought to achieve gains in sensor performance by using MIR QCLs as the optical source. MIR light interacts strongly with many molecules because photons in this portion of the spectrum can excite the fundamental vibrational and rotational modes of many of these molecules. The resonant excitation of these modes results in large optical absorption coefficients. The change in the intensity of the light passing through the gas depends exponentially on the absorption coefficient and the OPL; increasing the interaction of light with the gas under test improves the sensor performance. Figure 1a depicts optical absorption for light passing through a gas under test and Figure 1b is a schematic of the sensor in this project incorporating a RAC and a MIR QCL.

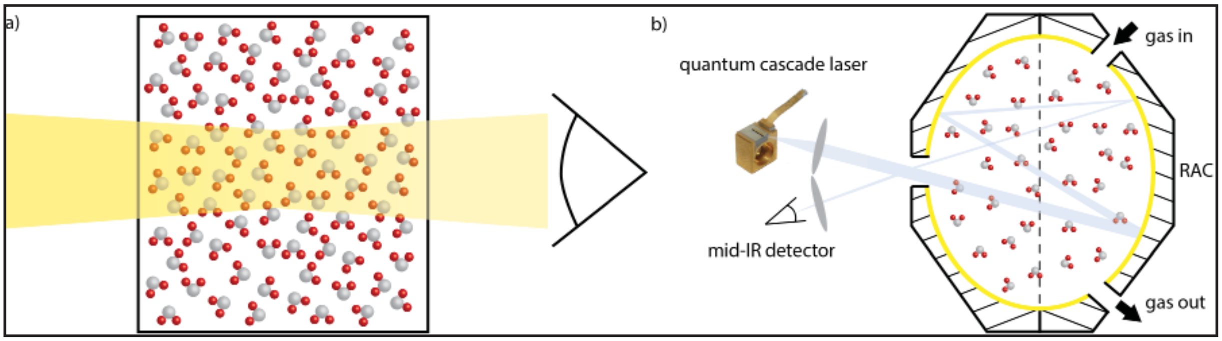


Figure 1: (a) Schematic of the change in intensity of an optical beam due to optical absorption; (b) Schematic of a RAC used as a sensor based on direct optical absorption sensing. The optical beam is depicted in blue. The focusing behavior inside the cavity is a result of the RAC design.

This research advances the goals of ALERT by developing technologies to detect airborne signatures of explosives including, for example, the vapor from triacetone triperoxide (TATP). The project leverages our expertise in MIR materials, detectors and sources to create optical sensors for this portion of the spectrum. Our work compliments other projects within ALERT that focus on optical detection using MIR QCLs (R2-C.2: Multiplexed Mid-Infrared Imaging of Trace Explosives and R3-C: Standoff Detection of Explosives: Mid-infrared Spectroscopy and Chemical Sensing) and benefits from research within ALERT that focuses on other sensors for vapor phase detection (R2-B.2: Portable, Integrated Microscale Sensors (PIMS) for Explosives Detection).

The societal benefits of this project included the development of optical sensing technologies for homeland security that have dual use in fields such as law enforcement, medicine, industry and agriculture. A product of this research is the dissemination of results to the MIR and broader scientific communities via peer-reviewed publications. The project included the training of undergraduate and graduate students in technologies relevant to the HSE. To this end, a relationship with Sandia National Laboratories (SNL) has been cultivated to support students from the PI's research group in internships. Finally, we also engaged local students through educational outreach events.

B. Biennial Review Results and Related Actions to Address

B.1 Detection Limits

The report indicates that we will demonstrate a detection sensitivity of 1 ppm using a single wavelength quantum cascade laser, RAC multipass gas cell, and detector. The reviewers indicated that a detection limit of 1 ppm may not be suitable for the needs of ALERT.

We want to emphasize that a level of detection of 1 ppm is only for the system we described operating with laser powers on the mw-level. The level of detection is limited by the relative intensity noise of the quantum cascade laser/detector combination. **We have a number of strategies to increase the level of detection to sub-10 ppb level.** This detection limit is the same as systems employing large-volume astigmatic multipass cells. The simplest approach to realize this level of detection are: (1) Increasing the optical power to tens of milliwatts, (2) normalizing the intensity of the pulse exiting the gas cell by monitoring the pulses emitted from the rear facet of the laser resonator (or via a beam splitter), and (3) increasing the optical path length.

These approaches can be implemented individually and together in our system.

Other strategies for achieving similar or better detection levels exist, including wavelength tuning and multiple wavelengths. The results of Year 3 will enable us to focus on additional improvements to the level of detection in this compact optical sensor. If time and resources permit, we will explore these other approaches too.

B.2. TATP is a model explosive

The progress to date has focused on a single wavelength laser for the detection of TATP. TATP is a model explosive that was selected for the initial work because it is a relevant to the DHS enterprise, and an appropriate QCL can be used for both TATP and acetone. Acetone sensing is performed in our UND laboratory, and TATP sensing will be done in collaboration with the team at Purdue. **The gas cells developed in this program can be used with lasers operating at other wavelengths (visible, near infrared, and mid-infrared) for the detection of vapor phase trace explosives other than TATP; for example, diacetone diperoxide (DADP), tetraacetone tetraperoxide (TRARP), hexamethylene triperoxide diamine (HMTD), and explosive precursors such as ammonia and peroxide.** Additionally, the multipass cells are dual-use with applications ranging from detection of breath analysis, environmental protection, and industrial process control.

B.3. Prior work in literature

Previous experimental work on 3-dimensional rotationally asymmetric cavities is limited to work from Claire Gmachl's group at Princeton University. The group demonstrated a rotationally asymmetric cavity with meter-length optical path lengths. This previous work employed numerical and optical experiments to **demonstrate that such a cell is viable**; however, the overall design and selection of ray trajectories for this type of highly compact multipass cells has been primarily exploratory and empirical. The design of these cells is complicated because many of the basic assumptions in cavity design do not apply—there is no body of work that describes the design or behavior of these optical cavities. We are applying techniques from dynamical systems theory and differential geometry to better develop an understanding of rotationally asymmetric cavities, and engineer superior devices.

There is substantially more work on deformed semiconductor microresonators for semiconductor lasers. These 2-D rotationally asymmetric resonators were pursued to reduce the laser threshold and control the far-field emission. **The resonators (microns in dimension) are in no way appropriate for gas cells**, as they are small semiconductors devices. Furthermore, the design of the 2-D resonators is significantly less complicated than our 3-D cavities because there are less degrees of freedom, thus there is very little prior work to draw upon.

B.4. System Cost

Concern was expressed over the cost of quantum cascade lasers. Indeed, it is true that quantum cascade lasers are more expensive than commercially available diode lasers. This is due in part to less time for maturation of the technology and lower demand. As the mid-infrared application space continues to develop and more companies engage in quantum cascade laser production, the cost is expected to decline dramatically (~1 order of magnitude). In a private conversation with a leading supplier of mid-infrared devices that incorporate quantum cascade gain media, the CEO indicated that they expect quantum cascade lasers to be available to companies at a cost of approximately $100 per device.

The PI (Hoffman) has collaborations with Thorlabs and Northrop-Grumman, companies interested in the development of quantum cascade lasers and associated technologies.

Through discussion following the Biennial Review process, ALERT requested and received authorization to use funding from the ALERT Science and Engineering Workforce Development Program (SEWDP) (formerly known as the ALERT Career Development Grant Program) to support graduate students who were working on cut projects such as this for up to two years in an effort to allow the students to graduate as planned. Galen Harden, a PhD student working on this project is expected to receive stipend support during the 2016/2017 school year.

C. State of the Art and Technical Approach

C.1. Introduction

Optical detection technologies are promising for trace gas detection because the overall system can be sensitive, compact, easy-to-operate, and inexpensive. Optical detection using MIR light offers improved sensitivity because MIR photons excite the fundamental vibrational and rotation modes of many molecules of interest. These resonant interactions result in large molecular optical absorption cross-sections at MIR wavelengths. The intensity of an optical beam that passes through a gas containing absorbing molecules is exponentially reduced due to absorption. The difference between the initial intensity and the final intensity of the beam can be used to quantify the concentration of absorbing molecules in the air sample under test. Furthermore, since the molecules have distinct absorption spectra, the type of molecule can also be determined by using many wavelengths of light.

The change in intensity of the optical beam is also influenced by the OPL. The Beer-Lambert Law, which describes the change in intensity for an optical source that passes through an absorbing medium (see Fig. 1a), is given by $I_T = I_o e^{-aL}$, where I_T, I_o, a, and L are the transmitted intensity, initial intensity, absorption coefficient, and OPL, respectively. The absorption coefficient depends on the attenuation coefficient, a molecular constant and a value that is relatively large in the MIR compared to optical frequencies and the number density. This project aims to create cavities with long OPLs, so as to enable the detection of a small number of molecules of interest.

We estimate that our RAC can achieve better than 1 ppm detection sensitivity of TATP in a RAC about the size of a baseball (1.5" cavity radius) and a mid-infrared quantum cascade laser. Our calculations are based on the measured relative intensity noise of a quantum cascade laser and thermoelectrically cooled mercury cadmium telluride detector. An advantage of the RAC over other gas cells is that this sensitivity can be achieved in a small gas cell. To compare RACs to other multipass cavities, we compare the ratio of the OPL to the cavity volume as a figure of merit (FOM). A standard Herriott cell has a FOM of 4.7 cm^{-2}, while a custom Herriott cell designed for minimal volume exhibits a FOM of 14.7 cm^{-2}. The RACs in this program should exhibit FOMs greater than 20 cm^{-2} and as large as 40 cm^{-2}; a marked improvement over existing technologies.

The use of MIR light for trace detection is being pursued in many fields. Prior work in the MIR has demonstrated the potential of optical detection of explosives using QCLs [1-3]. Our approach aims to advance this work by developing new multipass gas cells and pairing them with QCLs to realize sensitive detectors capable of unattended operation.

C.2. State of the Art

Cavities similar to the RACs designed in this project are not commercially available. Furthermore, there is little prior research in this area. A small body of work that initially demonstrated a rotationally symmetric cavity (RSC) and an RAC constitute all prior work [4-6]; there is a larger body of work on 2D chaotic microresonators [7-10]. In the prior work on RSCs and RACs, engineering the cavities and selecting appropriate trajectories was primarily exploratory and empirical. Our effort goes beyond the initial demonstration by engineering properties of the cavities and quantifying the influence of cavity geometry on properties such as OPL, GFT and stability, and using RACs for the trace detection of explosives.

Inside of ALERT, this project is unique in that we aim to develop new optical cavities; none of the other projects employing optical detection use optical cavities. At the same time, our project complemented other efforts within ALERT that use optical sensing and MIR technologies. We already work closely with Prof. Howard's group (R2-C.2), as they use equipment in our laboratory, and I have trained some of his graduate students in MIR measurements.

C.3. Our Approach

Proper modeling of the RACs is essential to achieving long OPLs and commercially available software is not appropriate for the cavities explored in this research. To support the objectives of this project, we have developed design tools for calculating the trajectories of arbitrary cavity shapes. The tools are coded in MATLAB and able to scale with the number of available cores on the CPU. Our code includes a primary function to calculate the trajectory of a beam given a cavity shape, input position, and input wavevector (momentum). The design toolbox also includes functions to analyze various aspects of the calculated trajectories, including computational error, beam size, eccentricity, and OPL.

The optical beam path through the cavity is modeled by calculating each reflection of a beam as it traverses the cavity. Unlike most design software, our calculations do not invoke the paraxial approximation, allowing for compact cavity designs. At every reflection, the spatial coordinates of the reflection are calculated using Newton's Method, and a simple linear transformation is used to calculate the wavevector for the reflected beam. Our code calculates the trajectory of 13 rays distributed in a ray bundle. Figure 2a on the next page shows the distribution of the ray bundle comprising 12 rays distributed around a central ray. The 12 rays forming the perimeter of a circle allow us to calculate properties of the beam, such as spot size, focusing and eccentricity, and to model the behavior of a beam that is converging or diverging as it enters the RAC.

The cavities examined in this project are spherical cavities with two quadrupole deformations. Figure 2b defines the angles used to describe the cavities that are given by the following equations:

$$x(\phi,\theta) = \frac{R_0\left[1+\epsilon_{yz}\cos 2\theta'\right]\sin\theta'\left[1+\epsilon_{xy}\cos 2\phi\right]\cos\phi}{1-\epsilon_{xy}}$$

$$y(\phi,\theta) = \frac{R_0\left[1+\epsilon_{yz}\cos 2\theta'\right]\sin\theta'\left[1+\epsilon_{xy}\cos 2\phi\right]\sin\phi}{1-\epsilon_{xy}}$$

$$z(\phi,\theta) = R_0\left[1+\epsilon_{yz}\cos 2\theta'\right]\cos\theta'$$

$$\theta'(\phi,\theta) = \frac{\pi}{2} - \tan^{-1}\left[\frac{1-\epsilon_{xy}\cot\theta}{1+\epsilon_{xy}\cos 2\phi}\right]$$

Here, $\in_{yz}$ and $\in_{xy}$ are the magnitude of the deformations in the yz and xy planes, respectively, and their values can range from 0 to 1. When both of the deformations are set equal to 0, the equation defines a sphere of radius R_0. These general cavity shapes are similar to those used in [4, 5]. Figure 2c depicts the calculated trajectory for the central ray in the ray bundle over 200 reflections for $\in_{yz} = 0.02$ and $\in_{xy} = 0.07$.

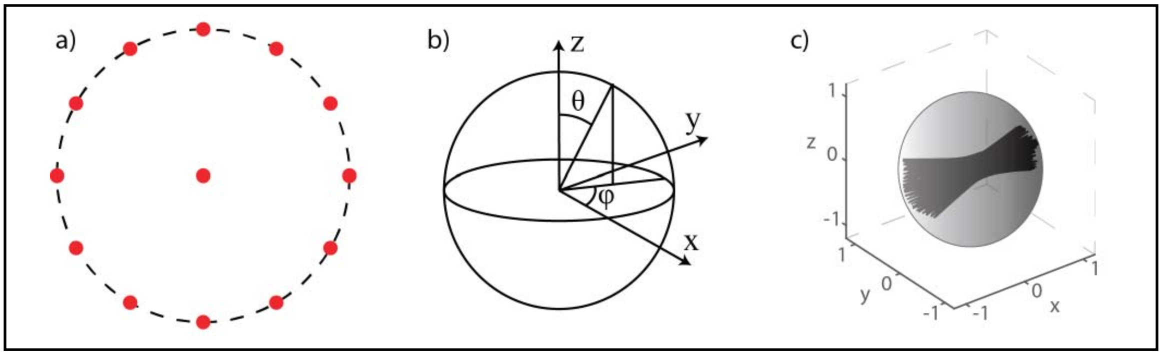


Figure 2: (a) Distribution of the 13 rays in a ray bundle. (b) Definition of the direction and angles for a RAC. (c) 3D image of the real-space trajectories of a RAC with ϵ_{xy} = 0.02 and ϵ_{yz} = 0.07.

The real space trajectories are useful for visualizing the distribution of light inside of the gas cell and are used in the design process to ensure that the beam trajectories do not overlap with the seam between the two halves of the fabricated gas cell (the dotted line in Fig. 1b shows the separation between the halves). In our models, the real space trajectories are useful for calculating the OPL and the catacaustic—the envelope of the rays after many reflections off of the cavity walls. The OPL for the ray trajectory shown in Figure 2c is 7.2 m for a cavity R_0=5.08 cm.

We want to emphasize the effort that we have put into ensuring efficient and low-error calculations of the ray trajectories. Because a principle aim of this project is to study RACs, which have a large design space, it is imperative that calculations of the cavity properties be efficient and accurate. Our code is written in MATLAB and uses techniques from Hamiltonian mechanics [11]. Additionally, the code can scale to the number of processors/cores available, enabling near-linear scaling with additional computing power. We are able to calculate 1000 reflections for a given cavity geometry in seconds on a desktop computer, enabling us to scan cavity parameters such as deformations, input position, and input wavevector. Our code also contains subroutines to monitor error in the calculated reflection; our error tolerance is typically set to 10^{-12} deg. in the reflected angle. This is noteworthy because our code does not reproduce some published results.

Our design toolbox also includes phase space representations of the trajectories that are useful for exploring the complex design space, and understanding the real space catacaustics. Figure 3 on the next page shows the phase space representation, called a surface of section (SoS), for 3 cavities with different geometries. The SoS comprises 20,000 points from reflections inside the cavity for a range of input conditions (position and wavevector). In the plot, χ is the angle of reflection, and θ is as depicted in Figure 2b.

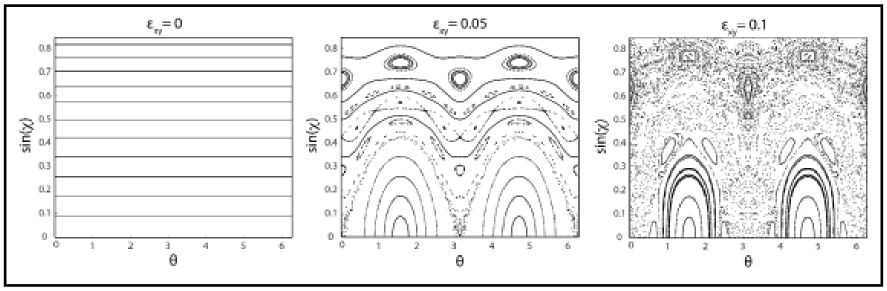


Figure 3: SoS for RACs with different deformations parameters: (a) ϵ_{xy} = 0 (a sphere); (b) ϵ_{xy} = 0.05; and (c) ϵ_{xy} = 0.1. The regions filled with lines that appear continuous correspond to normal trajectories and the regions filled with scattered points correspond to chaotic trajectories.

The SoS is helpful because it can be used to identify favorable ray trajectories. The SoS in Figure 3c displays two general types of behavior: (1) quasi-continuous curves, and (2) distributed points. These two regions characterize ordinary and chaotic behavior, respectively. For the work in this project, we select trajectories that display ordinary behavior (i.e. a small perturbation in the input conditions resulting in a small perturbation in the output conditions). It is important to note that even though these trajectories are ordinary in their behavior, their properties are influenced strongly by the cavity design, and are very different from those in a simple sphere; for example, we can engineer stable trajectories and GFT. The SoS is influenced by the cavity design. Figure 3a-c shows the SoS for several RACs, demonstrating the transition from a perfect sphere with no chaotic behavior to an RAC with a phase space dominated by chaotic behavior.

In this project, we studied the ray trajectories in RACs using techniques from dynamical systems theory to determine cavity geometries and ray configurations that result in long and stable optical paths. Distinct ray trajectories are possible for any combination of cavity deformation parameters, input position of the beam, and direction at which the beam is injected into the cavity. An ideal trajectory will have a long OPL inside the cavity. Additionally, the beam that is input will remain small compared to the size of the cavity so that it will be able to exit through the hole that has been drilled for it. The beam must also remain relatively circular in the cross section, or else a significant portion may not exit. Furthermore, no portion of the input beam should exit the cavity before the designed path length has been reached, and the trajectory must remain away from the gas input and output ports, so that these do not interfere with the reflections. Previous work based on RAC multipass cells, particularly the selection of appropriate ray trajectories, was primarily exploratory and empirical. Additionally, little attention was paid to engineering the GFT and spot size/shape. We have developed a systematic approach to engineering cavity behavior. This work resulted in a poster that was presented at the Conference on Lasers and Electro-Optics (CLEO) and a publication in Optics Express.

To engineer the OPL and GFT of RACs, we use our design toolbox to calculate trajectories of ray bundles comprising 13 beams (see Fig. 2c) for many cavity deformations, $\in_{yz}$ and $\in_{xy}$, and input beam conditions. This is possible because our code is efficient and we select a subset of all trajectories. An example trajectory is shown in Figure 2c, because such trajectories will not scatter off of the seam between the two cavity halves. We first analyze the beam bundles using the real space trajectories to determine cavity deformations that give the desired GFT and evolution of the spot size and shape. Panels (a), (b), and (c) of Figure 4 depict metrics for the GFT, spot area, and major axis versus the two cavity deformations. The white cross indicates the selected deformation parameters.

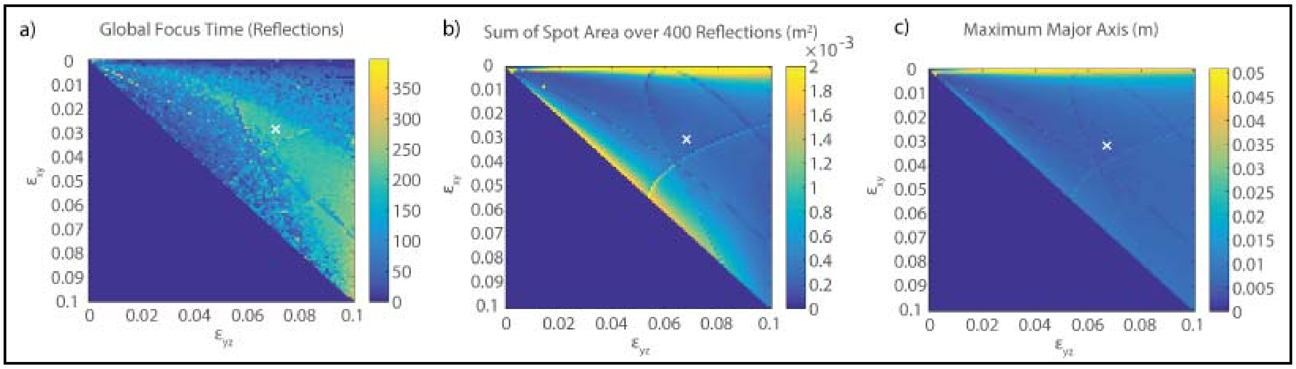


Figure 4: (a) GFT in number of reflections versus the cavity deformation parameters. (b) Sum of the beam spot size over all reflections for a total of 400 reflections. (c) The maximum length of the major axis of the beam over 400 reflections.

With the cavity deformation set, we calculate the SoS and select a quasi-periodic curve (lines that appear continuous in the SoS) with a long length in the phase space. Selecting a curve with a long length decreases the density of points in phase space and improves the OPL. Once a trajectory is selected, we calculate the orbit in real space (see Fig. 5a on the next page) and select the entrance port by finding areas with low point density, as in Figure 5b; we also select an exit port if needed. Selecting the entrance port defines the position and wavevector of the incident beam. Using this procedure, we designed a cavity with a GFT of 300 reflections and an OPL of 7.2m that would fit inside a sphere with a radius of 2.1”. Doubling the cavity dimensions more than doubles the OPL because the cavity is able to support more reflections (373 reflections with OPL of ~18m); this is one example of the nonlinear behavior that complicates the design and optimization of these cavities. This engineering is the topic of a manuscript that was published in Optics Express.

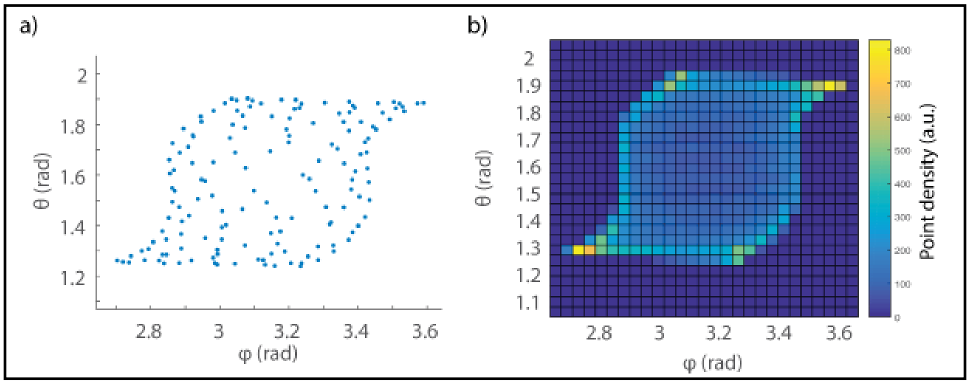


Figure 5: (a) Real-space trajectory plotted for the first 200 points using the azimuthal and polar angles from Fig. 2. (b) Density plot of Fig. 5a after 5000 reflections.

To study the stability of the RAC, we note that light reflecting off the surface of the cavity is very similar to the trajectory of a free particle bouncing elastically off of a boundary. This dynamical system can be described using the formalism of classical mechanics [12-16]. To study the stability of a selected trajectory, we apply a linear stability analysis. Linear stability describes how small perturbations to the original trajectory affect how the beam travels through the RAC [13]. This approach allows us to analytically study the relationship between the geometry of the cell and the stability of its ray trajectories. A brief summary of our approach follows.

Our implementation of the linear stability analysis relies upon mathematical theorems for a class of time-invariant physical systems. Because of these theorems, we are able to significantly reduce the complexity of the problem by studying the dynamics of a map in the intersection of two hypersurfaces in phase space; the two hypersurfaces are defined by constant energy curves and the reflection coordinates for all reflection (bounces) in a given trajectory. This mapping reduces the dimensionality of the dynamics from six (three position and three momentum coordinates) to four (two position and two momentum coordinates). The resulting map from this reduction is called the billiard map. It is in this reduced map we build the monodromy matrix, a linear operator in the tangent space of the billiard map that defines how perturbations stretch and contract in each bounce. The stability of the trajectory can be quantified by studying the eigenvalues and eigenvectors of the monodromy matrix. To further simplify this study, we use the fact that the billiard map, as in classical mechanics, is symplectic. This means that it preserves an area in phase space under evolution. Using this property, we can reduce the study of what would be four independent eigenvalues to only two stability parameters, which allows for visual analysis and comparison. Using this methodology, we can then systematically compare the stability of specific trajectories in an invariant manner.

Using the approaches outlined above, we designed a RAC with $\in_{yz} = 0.02$ and $\in_{xy} = 0.07$. The “radius” of the cavity is approximately 2” (the longest dimension is slightly larger due to the deformation parameters). The designed RAC was input into an AutoCAD and milled into copper using precision milling equipment. The inside surface of the RAC was coated using metals (100/300 nm Ti/Au) deposited by electron beam evaporation in the University of Notre Dame (UND) Nanofabrication Facility. The second generation RAC was designed, fabricated, and characterized. Photographs of the Au-coated RAC are shown in Figure 6. Trajectories up to 15 m have been measured in the RAC using the method described below and we believe that even longer optical trajectories are possible.

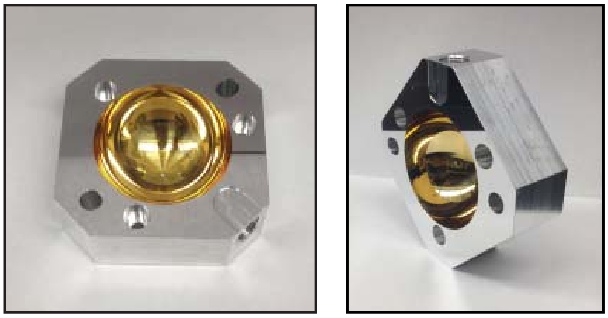


Figure 6: Photographs of one half of the second-generation RAC. The RAC was fabricated in aluminum and the cavity was coated with gold. The gas port and cell alignment holes are visible in the photographs.

The OPL of the cavities are characterized using time-of-flight measurement, depicted in Figure 7a. For such measurements, a diode laser is current modulated, resulting in a pulsed output. The amplitude-modulated optical beam is focused into the RAC, and the output beam, after traversing the RAC, is focused onto a fast rise-time Si detector. The train of pulses is recorded on a 40 GHz Lecroy digital oscilloscope. The beam is then aimed at the side in the RAC by translating the cavity, and focused onto the same detector. The difference in the time of flight enables a calculation of the difference between the optical paths. Since the external optical path can easily be measured, the OPL inside of the RAC can be determined. Initial characterizations were performed using a calibrated OPL of 52 cm. The Si detector voltage versus time is shown in Figure 6b; the time difference between paths (1) and (2) in Figure 7a is measured relative to the current source trigger. We measure a time difference of 1.7 ns for the two path lengths, which corresponds to an OPL of 51 cm—in excellent agreement with the known path length.

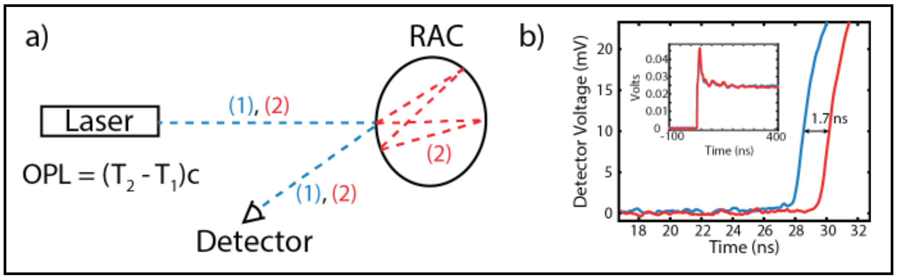


Figure 7: (a) Schematic of the time-of-flight setup. A pulsed laser has two possible paths (1) and (2) that can be selected by translating the cavity. Path (1) is reflected off of the RAC external surface and path (2) transits the RAC. The output from the fast rise time Si detector (15 ns) is monitored on a 40 GHz oscilloscope. The OPL of the RAC is given by the time difference between paths (1) and (2) multiplied by the speed of light. (b) Optical characterization using the method in (a) for a calibrated 53 cm path length. The color of the traces corresponds to the time delay for the paths shown in (a).

A detailed analysis of our experimental setup gives an error of 2 cm that is limited by trigger jitter. This error is well within a tolerable amount for the purposes of characterizing RACs. The same experimental scheme can be used to characterize the cavity with a mid-infrared laser, though very little difference is expected. Our laboratory is equipped with the necessary QCLs, pulsed current/voltage driver, optical elements, and high speed detectors for mid-infrared measurements.

We have also characterized a custom QCL for use in this project. Our group has expertise in the design, fabrication, and characterization of QCLs [17-20]. The QCL for this project was designed to emit at 1200 cm^{-1}. This particular wavelength was selected because there is overlap between absorption features due to acetone and TATP, as seen in Figure 8a. The benefit of working at this wavelength is that acetone, a precursor to TATP, is readily available in our laboratory for testing, and later, we can use the same laser to detect TATP. Additionally, this wavelength range is favorable because the region is relatively free of interference due to water and CO_2 absorption.

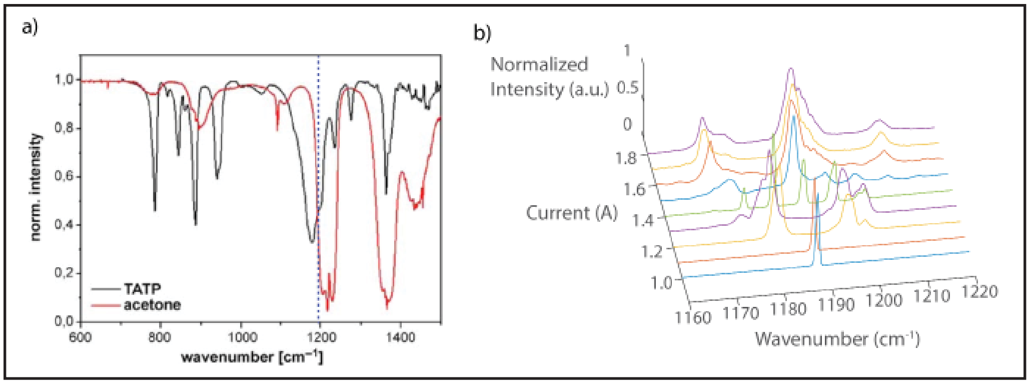
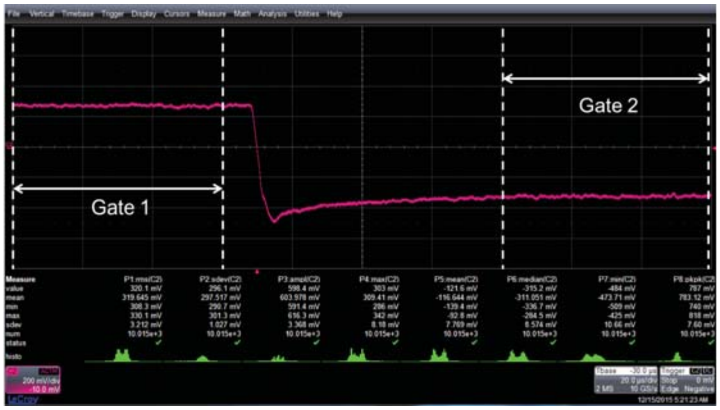


Figure 8: (a) FTIR spectra of TATP and acetone measured using an FTIR from [3]. The vertical, dashed line indicates the emission wavelength of the QCL in (b); (b) Emission measured from a QCL operated in CW mode at 298K using a FTIR at various drive currents.

The tested laser has a Fabry-Perot resonator and is capable of emitting at room temperature in continuous wave (CW) mode with 100s of mW of output power; 450 mW at 298K on a continuous flow liquid nitrogen cryostat; and ~200 mW on a thermoelectric cooler (TEC) set to 298K. The emission spectrum of the laser mounted to a TEC at 298K and operated in CW mode is shown in Figure 8b. We performed these measurements on our custom v80v Bruker vacuum spectrometer using a room temperature DTGS detector. Near lasing threshold, the emission is single-peaked and centered near 1190 cm^{-1}. As the drive current is increased, the spectrum becomes multimode. We anticipate that for this project, we will be able to operate the laser at currents close to the threshold, thus avoiding multimode emission. To reduce device heating, we can run the laser in pulsed mode with a low duty cycle (<0.1%). The advantage of the pulsed mode of operation is that we can significantly reduce the size of the optical source by removing the TEC. The disadvantage is that the spectrum in pulsed operation is multimode, comprising dozens of Fabry Perot modes. If necessary in the future, we can fabricate pulsed, single-mode distributed feedback (DFB) lasers that emit at the same wavelength using the 100 kV electron beam lithography writer available in the UND Nanofabrication Facility.

We also characterized the relative noise intensity (RIN) of the MIR QCL and detector system. Figure 9 shows the output of the detector as a MIR QCL is focused onto the detector element; the laser is attenuated using a holographic KRS-5 polarizer to avoid saturating the detector. The pulse is integrated over the two gated regions (indicated by white arrows on the pulse schematic) and statistics are collected over 10,000 pulses. The mean pulse height is 950.4 mV and the standard deviation is 1.74 mV. The calculated RIN for the laser, lens, and detector system is -150 dB/Hz$^{0.5}$. Additionally, the long term drift of the system was also characterized. For these measurements, the laser was continuously run in pulsed mode and data was sampled every 5 minutes for 6 hours. The total drift was less than 1.1 mV (0.1% of the attenuated pulse height). This long term drift is not problematic for sub-10 ppb detection and if needed, can be improved by monitoring the drifts in the pulse intensity using a beam splitter, or by measuring emission from the back facet of the laser cavity.



Measure	P1:rms(C2)	P2:sdev(C2)	P3:ampl(C2)	P4:max(C2)	P5:mean(C2)	P6:median(C2)	P7:min(C2)	P8:pkpk(C2)
value	320.1 mV	296.1 mV	598.4 mV	303 mV	-121.6 mV	-315.2 mV	-484 mV	787 mV
mean	319.645 mV	297.517 mV	603.978 mV	309.41 mV	-116.644 mV	-311.051 mV	-473.71 mV	783.12 mV
min	308.3 mV	290.7 mV	591.4 mV	286 mV	-139.4 mV	-336.7 mV	-509 mV	740 mV
max	330.1 mV	301.3 mV	616.3 mV	342 mV	-92.8 mV	-284.5 mV	-425 mV	818 mV
sdev	3.212 mV	1.027 mV	3.368 mV	8.18 mV	7.769 mV	8.574 mV	10.66 mV	7.60 mV
num	10.015e+3	10.015e+3	10.015e+3	10.015e+3	10.015e+3	10.015e+3	10.015e+3	10.015e+3
status	✓	✓	✓	✓	✓	✓	✓	✓

Figure 9: Voltage pulse for a 1000 ns pulse of a MIR QCL focused onto a cooled MCT detector. The voltage is integrated over the two gates (indicated by dashed lines) and used to calculated the RIN.

Finally, we have also developed an idea to use an MIR QCL with an integrated Schottky diode as both the source and detector with the RAC as part of our discussions with Dr. Michael Wanke at SNL. This unique optical device would be able to detect small changes in the phase and amplitude of light that interacts with a sample under test. Such a device could enable further improvements in the detection limits of the optical sensor. Additionally, the device may have other applications within ALERT, including use as a handheld sensor for detecting liquid and solid explosives. Preliminary devices have been grown via molecular beam epitaxy, fabricated, and tested. Radio frequency measurements have demonstrated nonlinear mixing in the integrated diode, demonstrating that our devices work. Together with Dr. Wanke, we submitted a collaborative project to the ALERT Call for Whitepapers in the summer of 2016. The proposal aims to improve the nonlinear mixing in the devices by engineering the optical mode and the quantum wavefunctions, and to use the devices for stand-off detection of explosives. The project involves a student internship at SNL.

D. Major Contributions

The following is a list of contributions that this project has made to the ALERT research program.

D.1. Year 3

- Studied stability of RACs and designed, fabricated, and characterized a RAC with a stability better than the state-of-the-art asymmetric Herriot gas cell. A publication has been accepted in Optics Express on this RAC, and we presented our work at the Conference of Lasers and Electro-optics.
- Measured optical path lengths greater than 15 meters. This is greater than the minimum distance required to meet the sensitivity limits specified by our calculations.
- Conducted detailed study of the relative intensity noise of a custom quantum cascade laser, laser driver, and cooled detector to improve the detection limits of the sensor.
- Conducted single and multi-pass absorption measurements of acetone using RAC and characterized sensor system.
- Submitted one manuscript to Optics Express, and a conference abstract to the Conference on Lasers and Electro-optics (CLEO)—the premier optics conference in the US. The manuscript is under review and the peer-reviewed conference paper has been accepted for presentation.

D.2. Year 2

- Designed and characterized custom QCL for MIR trace detection of TATP and acetone. The QCL and all of our control electronics and detectors are available to other members of ALERT and reside in our UND facility.

- Developed an algorithm and numerical code for linear stability analysis of RACs. The code will be shared via the Creative Commons License.
- Designed and fabricated a second-generation RAC. The RAC will be valuable for the questions in this project and accessing the broader ALERT question of: "How do we properly deliver gas samples to the various detectors being developed in the center?"
- Developed a process for engineering OPL, GFT, and RACs. Our work on engineering the GFT was a consequence of a discussion with Eos Photonics, an ALERT Industry Partner.

D.3. Year 1

- Characterized RAC and identified problems with fabrication.
- Created optical setup for characterizing OPL using time-of-flight measurements.
- Designed and fabricated first-generation cavity.
- Developed models and efficient algorithms for RACs (available via Creative Commons License). Our software and algorithms, useful beyond RACs, are available to ALERT academic partners and the broader HSE community.

E. Milestones

The following is a list of milestones that must be accomplished for this project to reach its objectives:

1. Successfully characterize second-generation RAC using optical laser and QCL, and demonstrate cavity modes with OPLs > 15m, a total cell volume < 150 cm^3 and greater than 98.5% reflected power per reflection. This milestone has been achieved.
2. Demonstrate and quantify optical sensing using MIR QCL.
3. Demonstrate optical detection with acetone and characterize sensor limits. This milestone has been achieved.
4. Demonstrate optical detection with TATP and characterize sensor limits.
5. Investigate methods for sample delivery and sensor deployment.

F. Future Plans

The project was not selected to continue as part of the ALERT COE. We have requested a no-cost extension (NCE). During the NCE we will continue measuring the designed RACs and characterize the optical system for trace gas detection.

1. We will use the second-generation cavity to perform trace detection of acetone. We will characterize detection limits of the optical sensor. If time and funding allows, we will also perform trace detection of TATP with the assistance of other ALERT academic partners (primarily the researchers at Purdue). UND's proximity to Purdue enables us to travel to their testing facilities and work with their experts on safely testing for TATP if needed.
2. We will use our RAC to explore methods for gas delivery to the multipass cell and characterize the RAC sensor in realistic sensing environments.
3. We will begin working towards developing QCLs with integrated Schottky diodes that can be used with the RAC. Through our collaboration with SNL, we have access to QCL material that can be used

for this purpose. We will fabricate the devices in the UND Nanofabrication Facility and test the sources in my laboratory.

III. RELEVANCE AND TRANSITION

A. Relevance of Research to the DHS Enterprise

1. We are developing new multipass gas cells for optical detection of trace amounts of explosives or their precursors by analyzing samples of air. Identifying trace amounts of explosives using optical technologies is one way to identify explosives on people, bags, vehicles, animals, etc. Our project studies the basic science of optics in rotationally asymmetric cavities to design low-volume, multipass cells for trace gas detection. The goal is to demonstrate an RAC with a path length greater than 10 meters, a total cell volume less than 50 cm^3 and greater than 90% reflected power per reflection. This OPL will enable detection of TATP at a sensitivity of 1 ppm with a FOM (OPL/cell volume) greater than 20.
2. A challenge related to optical sensing is gas delivery. To address this challenge as a center, ALERT conducts research in many modes of detection, including approaches that do not require gas delivery. Our project will address this challenge by demonstrating optical detection of trace amounts of acetone and TATP using an RAC with a QCL and MIR detector at sensitivity levels better than 1 ppm in the laboratory. We will then collaborate with other ALERT academic partners to test the sensor in more “real-world” scenarios, enabling testing of various gas delivery methods and strategies.

B. Potential for Transition

We envision using the RACs for MIR trace gas detection. Relevant to the HSE, we envision using these sensors as point sensors, or in a distributed network to detect explosives or their precursors. Potential deployment could include mounting the sensor into screening stations, such as conveyors for screening baggage or palletized shipping containers, and developing mobile platforms for sampling the headspace of large shipping containers that arrive at ports and small shipping containers that are placed on aircraft. These applications mitigate some of the challenges associated with the low vapor pressures of trace gases of interest because the gas is leaving a container and entering a controlled sampling space. The benefit of optical detection is that the sensors can run continuously, provide relevant-time information, and detect small concentrations. The RACs in this project are compact, reducing the overall instrument size, and making installation and mobile deployment easier for the end user.

We are in the planning stages with doctors and medical professionals at Yale University to use the gas cell for breath monitoring during surgery. While not directly relevant to the detection of explosives, such applications could have a major impact on the quality of care in battlefield hospitals and general surgery.

C. Data and/or IP Acquisition Strategy

The appropriate data to implement the methodology, and test the hypotheses and outcomes outlined in this project report are all acquired via simulation and measurement in my laboratory. My lab, which specializes in MIR and terahertz photonics, is equipped for the characterization of the RACs and QCLs detailed in this report. Optical detection of trace amounts of acetone will also be performed in my lab. For the detection of TATP, we will work with other academic partners within ALERT, particularly those at Purdue. We will work with Prof. Beaudoin to enable these collaborations. Prof. Beaudoin has already supplied solid samples to UND for testing.

D. Transition Pathway

The transition pathway for this project uses several mechanisms to engage potential customers, including: (1) publishing our design tools as open-source software (OSS) via the Creative Commons License; (2) publishing our work in high impact journals and presenting at the top conferences; (3) engaging in conversations with potential end users; and (3) training students for the workforce.

As part of this project, we designed custom design tools because commercial software that is appropriate for the design of RACs is not available. Our design tools efficiently solve the trajectories of light rays inside of an optical cavity of arbitrary design; most commercial software has restrictions on the cavity design. Our software includes tools for analyzing and studying individual trajectories and caustics, including, OPL, beam divergence, beam eccentricity, and more. The design software suite is hosted in a repository on Github. The code for calculating the optical trajectories has been included as supplementary information in our manuscript accepted for publication in Optics Express and is available to the broader optics community.

Transition is also accomplished by sharing the results of our work in high impact journals and conferences. Our work on analyzing the stability of optical trajectories in RACs was presented at the Conference on Laser and Electro-Optics (CLEO). CLEO is the premier optics conference in our field. Additionally, our work on engineering optical trajectories in RACs and modeling their stability has been accepted for publication in Optics Express.

In Year 2, we had a conversation with Mark Witinski, Ph.D., President Eos Photonics, about our RACs. During the conversation, Mark indicated that one of the more interesting aspects of our work was to engineer the GFT. After this conversation, we focused on improved methods for controlling and engineering the GFT. This included improving our design tools and reexamining our design methods. A new RAC based on these new ideas and tools was fabricated in Year 3 (see Fig. 6). The design of the cell is detailed in our manuscript accepted in Optics Express. This cell has allowed us to the milestones indicated as completed in Section II.E.

Finally, transition occurs via the training of students at both the undergraduate and graduate levels; my students are trained to be experts in optical and MIR technologies. All of the students involved in this project are aware of the broader scope of ALERT. My students participate in ALERT activities, including industry day, and educational outreach events.

E. Customer Connections

We have established a relationship with SNL. We have discussed potential areas for collaboration, including the development of a QCL with integrated Schottky diode that enables the optical source to also behave as an optical detector. Such a device could be integrated into our chaotic cavity, or serve as a handheld sensor for detecting explosives. We have discussed sending my ALERT graduate student to Sandia during the summer of 2016 (after the student has finished the PhD qualifying exams) to work in Dr. Wanke's optoelectronic laboratory. We have also discussed seeking funding through the Center for Integrated Nanotechnology (CINT), a US DOE User Facility. Such collaboration would be an excellent means for transitioning technology and our work. Our level of contact has been three conversations and a visit by Dr. Wanke at UND.

As already mentioned, we have also had two conversations with Dr. Witiniski of Eos Photonics. Eos Photonics makes tunable QCL arrays and is interested in our work because we are advancing the state of the art of MIR sensing. We have discussed the possibility of acquiring a demo unit of their QCL array for testing with our RACs or purchasing one at a reduced cost. The initial conversation was facilitated by Emel Bulat, the ALERT Industrial and Government Liaison Officer.

IV. PROJECT ACCOMPLISHMENTS AND DOCUMENTATION

A. Education and Workforce Development Activities

1. Course, Seminar, and/or Workshop Development

   An introductory course to Electrical Engineering for sophomore engineering students was instructed in 2016 (EE-20225: Introduction to EE). Enrollment for this course totaled 52 students in 2016. As part of the course development process, faculty were requested to submit potential labs for the students. I submitted a proposal for the creation of an optical spectroscopy laboratory incorporating some of the tools and elements presented by Professor McKnight of Northeastern University, and modules that my group has developed for outreach. Our laboratory was not selected for 2016, but we will continue to submit for this laboratory as the course curriculum is modified.

2. Interactions and Outreach to K-12, Community College, and/or Minority Serving Institution Students or Faculty

   Members of our group participated in outreach to local middle schools in Spring 2015. The volunteers interacted with the students during a day-long event, performing hands-on experiments and engaging the students in conversations about the importance of education and what it is like to do research. The event included a half-day follow-up field trip to Notre Dame for the students to visit active research laboratories. This annual event is sponsored by the Notre Dame SPIE Chapter, and the graduate students participating in this program are active members of the chapter. Prof. Hoffman is the faculty advisor for SPIE and Owen Dominguez is an officer in SPIE.

3. Training to Professionals or Others

   I am the UND faculty mentor for the International Society for Optics and Photonics (SPIE) and the IEEE Photonics Society and Electronic Devices Society Joint Chapter President. As part of the broader scope of this project, I am able to regularly engage graduate students and professionals across many disciplines, including those in electrical engineering, chemistry, chemical engineering and physics.

B. Peer Reviewed Journal Articles

Pending-

1. Harden, Galen; Cortes Herrera, Luis E.; Harter, Michael P.; and Hoffman, Anthony J. “Engineering Optical Behavior in Rotationally Asymmetry Cavities.” accepted Optics Express.

C. Peer Reviewed Conference Proceedings

1. G.H. Harden, L.E. Cortes-Herrera, and A.J. Hoffman. “Stability of Optical Trajectories in Rotationally Asymmetric Multipass Cells.” Conference on Lasers and Electro-optics, San Jose CA, June 2016.

D. Other Conference Proceedings

1. Cortes Herrera, Luis E., Harden, Galen, and Hoffman, Anthony J. “Engineering the linear stability of ray trajectories in highly compact chaotic multipass cells.” NDnano Undergraduate Research Symposium, Notre Dame, IN. July 2015.

E. Other Presentations

1. Seminars:
   a. A.J. Hoffman, “Advances in mid-infrared technologies: Rotationally asymmetric gas cells and

intersubband polariton emitters." University of Illinois Urbana-Champaign, December 2015.

2. Poster Sessions:
    a. G.H. Harden, L.E. Cortes-Herrera, and A.J. Hoffman. "Stability of Optical Trajectories in Rotationally Asymmetric Multipass Cells." Conference on Lasers and Electro-Optics, San Jose, 2016.
3. Briefings:
    a. A.J. Hoffman, "Mid-infrared Technologies for Optical Trace Detection," Air Force Office of Scientific Research, December 2015.

F. New and Existing Courses Developed and Student Enrollment

New or Existing	Course/Module/ Degree/Cert.	Title	Description	Student Enrollment
Existing	Course	**Fundamentals of Semiconductor Physics**	**Graduate-level course (description below)**	**10-15**

I instruct the graduate-level "Fundamentals of Semiconductor Physics" course every fall semester. Since joining the ALERT program, I have included material related to ALERT research in my course, such as quantum cascade heterostructures, quantum dots, and absorption spectroscopy. The course enrollment is typically 10-15 graduate students.

G. Software Developed

1. Algorithms
    a. The algorithms that we developed for efficiently solving the ray trajectories and stability have been included as supplementary information in our article that has been accepted for publication in Optics Express.

V. REFERENCES

[1] 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 vapor detection using a broadly tunable (6-8 um) optical parametric oscillator," Applied Physics B 75, 367-376 (2002).
[2] Dunayevskiy, A. Tsekoun, M. Prasanna, R. Go & C.K.N. Patel. "High-sensitivity detection of triacetone triperoxide (TATP) and its precursor acetone," Applied Optics 46, 6397-6404 (2007).
[3] C. Bauer, A.K. Sharma, J. Burgmeier, B. Braunschweig, W. Schade, S. Blaser, L. Hvozdara, A. Muller & G. Holl. "Potentials and limits of mid-infrared laser spectroscopy for the detection of explosives," Applied Physics B 92, 327-333 (2008).
[4] D. Qu, Z. Liu & C. Gmachl. "A compact asymmetric chaotic optical cavity with long optical path lengths," Applied Physics Letters 93, 014101 (2008).
[5] D. Qu & C. Gmachl. "Quasichaotic optical multipass cell," Physical Review A 78, 033824 (2008).
[6] D. Qu & C. Gmachl. in IEEE Sensors 2007.
[7] C.-L. Zou, F.-W. Sun, C.-H. Dong, F.-J. Shu, X.-W. Wu, J.-M. Cui, Y. Yang, Z.-F. Han & G.-C. Guo. "High-Q and Unidirectional Emission Whispering Gallery Modes: Principles and Design," IEEE Journal of Selected Topics in Quantum Electronics 19, 9000406 (2013).
[8] H.E. Tureci, H.G.L. Schwefel & A.D. Stone. "Modes of wave-chaotic dielectric resonators," Prog.

Opt. 47, 75-137 (2003).

[9] J.U. Nockel & A.D. Stone. “Rays and wave chaos in asymmetric resonant optical cavities,” Nature, 45-47 (1997).

[10] J.U. Nockel & A.D. Stone. in Optical Processes in Microcavities (eds R.K. Chang & A.J. Campillo) (World Scientific Publishers, 1996).

[11] V.I. Arnold. Mathematical Methods of Classical Mechanics. (Springer, 1997).

[12] K. Zhang. “Speed of Arnold disuffion for analytic Hamiltonian systems,” Invent Math 186, 255-290 (2011).

[13] J.E. Howard & R.S. MacKay. “Linear stability of symplectic maps,” Journal of Mathematical Physics 28, 1036 (1987).

[14] S.-J. Chang & R. Friedberg. “Elliptical billiards and Poncelet’s theorem,” Journal of Mathematical Physics 29, 1537 (1988).

[15] P.S. Casas & R. Ramirez-Ros. “The frequency map for billiards inside ellipsoids,” SIAM Journal on Applied Dynamical Systems 10, 278-324 (2011).

[16] P.L. Calvez & J. Wang. “Some Remarks on the Poincare-Birkhoff Theorem,” Proceedings of the American Mathematical Society 138, 703-715 (2009).

[17] Y. Yao, A.J. Hoffman & C.F. Gmachl. “Mid-infrared quantum cascade lasers,” Nature Photonics 6, 432-439 (2012). doi:10.1038/nphoton.2012.143

[18] P.Q. Liu, A.J. Hoffman, M.D. Escarra, K.J. Franz, J.B. Khurgin, Y. Dikmelik, X.J. Wang, J.Y. Fan & C.F. Gmachl. “Highly power-efficient quantum cascade lasers,” Nature Photonics 4, 95-98 (2010). doi:10.1038/nphoton.2009.262

[19] K.J. Franz, P.Q. Liu, J.J.J. Raftery, M.D. Escarra, A.J. Hoffman, S.S. Howard, Y. Yao, Y. Dikmelik, X.J. Wang, J.Y. Fan, J.B. Khurgin & C. Gmachl. “Short Injector Quantum Cascade Lasers,” Ieee Journal of Quantum Electronics 46, 591-600 (2010). doi:10.1109/jqe.2009.2030896

[20] M.D. Escarra, A. Benz, A.M. Bhatt, A.J. Hoffman, X.J. Wang, J.Y. Fan & C. Gmachl. “Thermoelectric Effect in Quantum Cascade Lasers,” Ieee Photonics Journal 2, 500-509 (2010). doi:10.1109/jphot.2010.2050304

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