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14. ABSTRACT It has long been recognized that the SMM/THz has a unique combinations of attributes that make it attractive as a basis for sensors. It is also well known that both the scientific and technical base for exploiting these attributes is small in comparison to other more mature spectral regions. This project involves three, mutually supporting, efforts: The first is to study and demonstrate techniques to extend the applicability of SMM chemical sensors; the second is to explore infrared – SMM double resonance as a basis for atmospheric remote sensing; and the third is to explore applications made accessible by high power vacuum electronics. Most recently, the high power EIK tube					
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Report Title

Techniques for SMM/THz Chemical Analysis: Investigations and Exploitation of the Large Molecule Limit

ABSTRACT

It has long been recognized that the SMM/THz has a unique combinations of attributes that make it attractive as a basis for sensors. It is also well known that both the scientific and technical base for exploiting these attributes is small in comparison to other more mature spectral regions. This project involves three, mutually supporting, efforts: The first is to study and demonstrate techniques to extend the applicability of SMM chemical sensors; the second is to explore infrared – SMM double resonance as a basis for atmospheric remote sensing; and the third is to explore applications made accessible by high power vacuum electronics. Most recently, the high power EIK tube from NRL became available again. With it we expanded the imaging efforts previously reported and incorporated hardware and software that made possible the construction of 3-D images that are largely free of speckle and that did not depend upon critically oriented targets.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
03/27/2013 36.00	Jennifer A. Holt, Mark A. Patrick, Colin D. Joye, Frank C. De Lucia. Elimination of speckle and target orientation requirements in millimeter-wave active imaging by modulated multimode mixing illumination, Journal of Optical Society of America, (12 2012): 2643. doi:
03/27/2013 38.00	Christopher F. Neese, Ivan R. Medvedev, Grant M. Plummer, Aaron J. Frank, Christopher D. Ball, Frank C. De Lucia. Compact Submillimeter/Terahertz Gas Sensor With Efficient Gas Collection, Preconcentration, and ppt Sensitivity, IEEE Sensors Journal, (08 2012): 2565. doi: 10.1109/JSEN.2012.2195487
03/27/2013 39.00	Dane J. Phillips, Elizabeth A. Tanner, Frank C. De Lucia, Henry O. Everitt. Infrared-terahertz double-resonance spectroscopy of CH ₃ F and CH ₃ Cl at atmospheric pressure, Physical Review A, (05 2012): 0. doi: 10.1103/PhysRevA.85.052507
03/27/2013 37.00	Douglas T. Petkie, Jennifer A. Holt, Mark A. Patrick, Frank C. De Lucia. Multimode illumination in the terahertz for elimination of target orientation requirements and minimization of coherent effects in active imaging systems, Optical Engineering, (05 2012): 0. doi: 10.1117/1.OE.51.9.091604
05/13/2010 4.00	Frank C. De Lucia. The Submillimeter: A Spectroscopist's View, Journal of Molecular Spectroscopy, (01 2010): . doi:
09/16/2010 8.00	F.C. De Lucia, D. T. Petkie, H.O. Everitt. A Double Resonance Approach to Submillimeter/Terahertz Remote Sensing at Atmospheric, Journal of Quantum Electronics, (02 2009): . doi:
09/16/2010 9.00	I.R. Medvedev, C. F. Neese, G. M. Plummer, F. C. De Lucia. Submillimeter spectroscopy for chemical analysis with absolute specificity, Optics Letters, (05 2010): . doi:
09/17/2010 10.00	B.P. Winnewisser, M. Winnewisser, I. R. Medvedev, F. C. De Lucia, S. C. Ross, J. Koput. Analysis of the FASSST rotational spectrum of NCNCS in view of quantum monodromy, Physical Chem Chem Physics, (02 2010): . doi:
10/16/2011 25.00	Ivan R. Medvedev, Christopher F. Neese, Grant M. Plummer, Frank C. De Lucia. Impact of Atmospheric Clutter on Doppler-limited Gas Sensors in the Submillimeter/Terahertz., Applied Optics, (06 2011): 3028. doi:
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Number of Papers published in non peer-reviewed journals:

(c) Presentations

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

02/28/2014 49.00 Mark A. Patrick , Frank C. De Lucia, Dane J. Phillips , Daniel L. Faircloth. Radar Cross Sections in the Shorter Millimeter-wave Region: Characterization and Calculations for Targets that include Rough Surfaces, Antenna Measurement Techniques Association. 09-OCT-13, . : ,

03/29/2013 44.00 Douglas T. Petkie , Jennifer Holt , Christopher F. Neese, Frank C. De Lucia, Ivan R. Medvedev, Bob D. Guenther . Terahertz Signature Modeling for Kill Assessment and Warhead Materials Identification, 2012 MSS Missile Defense Sensors, Environment and Algorithms . 25-OCT-12, . : ,

03/29/2013 42.00 Frank C. De Lucia. Physics, Applications, and the State-of-the-Art in the THz Spectral Region, Materials Week Columbus 2011. 13-SEP-13, . : ,

03/29/2013 47.00 Dane J. Phillips, Frank C. De Lucia, Henry O. Everitt. IR/THz Double Resonance Spectroscopy of Methyl Fluoride and Collision Partners self, N2, Ar, He, CO2, and Air, 67th Ohio State University International Symposium on Molecular Spectroscopy, June 18-22, 2012, Columbus, OH. 18-JUN-12, . : ,

03/29/2013 48.00 Frank C. De Lucia. From Spectroscopy to Sensors , Pittcon. 19-MAR-13, . : ,

TOTAL: 5

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):ReceivedPaper

10/18/2011 34.00 Frank C. De Lucia. PL-6: Spectroscopic systems and vacuum electronics in the submillimeter, 2010 IEEE International Vacuum Electronics Conference (IVEC). 18-MAY-10, Monterey, CA, USA. : ,

10/19/2011 33.00 D. J. Phillips , E. A. Tanner , H. O. Everitt, I. R. Medvedev , C. F. Neese , J. Holt, F. C. De Lucia. Infrared/Terahertz Double Resonance for Chemical Remote Sensing: Signatures and Performance Predictions, Terahertz Physics, Devices, and Systems IV: Advanced Applications in Industry and Defense. , Orlando, Florida, USA. : ,

TOTAL: 2**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

(d) ManuscriptsReceivedPaper

03/27/2013 35.00 Mark A. Patrick , Jennifer A. Holt, Colin D. Joye , Frank C. De Lucia. Elimination of speckle and target orientation requirements in millimeter-wave active imaging by modulated multimode mixing illumination, Journal of Optical Society of America (08 2012)

05/13/2010 1.00 Ivan R. Medvedev, Christopher F. Neese, Grant M. Plummer, Frank C. De Lucia. Submillimeter spectroscopy for chemical analysis with absolute specificity , (05 2010)

05/13/2010 6.00 Dane J. Phillips, Elizabeth A. Tanner, Henry O. Everitt, Ivan R. Medvedev, Christopher F. Neese, Jennifer Holt, Frank C. De Lucia. Infrared/Terahertz Double Resonance for Chemical Remote Sensing: Signatures and Performance Predictions, (05 2010)

TOTAL: 3

Number of Manuscripts:

Books	
<u>Received</u>	<u>Paper</u>
TOTAL:	

Patents Submitted

Patents Awarded

Awards

Mark Patrick: First Prize Student Paper at the AMTA National meeting 2013

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Corey Casto	0.12	
David Graff	0.21	
Yaser Helal	0.12	
James McMillan	0.02	
Mark Patrick	0.32	
FTE Equivalent:	0.79	
Total Number:	5	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Christopher Neese	0.16
FTE Equivalent:	0.16
Total Number:	1

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Frank De Lucia	0.09	
FTE Equivalent:	0.09	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
-------------	--------------------------

FTE Equivalent:

Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>

Total Number:

Names of personnel receiving PHDs

<u>NAME</u>

David Graff

Total Number: 1

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

There are two parts to this attachment. The first lists our Accomplishments and the second discusses Tech Transfer and Interactions.

ACCOMPLISHMENTS

This project involved three, mutually supporting efforts: The first was to study and demonstrate techniques to extend the applicability of SMM chemical sensors; the second (with supplemental funds from AMRDEC) was to explore infrared – SMM double resonance as a basis for atmospheric remote sensing; and the third (with supplemental funds from DARPA) is to explore the physical regimes made accessible by high power vacuum electronics in the SMM/THz.

I. Applications of SMM chemical sensors

Introduction: It has long been known that the SMM spectral region has a unique combination of properties that make it useful as the basis of sensor systems that range from astrophysical applications (there are now three ~\$1 B instruments in place) to chemical sensors and imaging. Interestingly, even though all of these applications have been known for many decades, only the exotic and expensive one-of-a-kind applications have a major foothold. Many of the others are approaching having a real world impact, but a combination of technical affordability, physical unknowns, and a need for appropriate system strategies remain impediments. This project addresses the latter two of these issues. Via Tech Transfer (addressed in the second part of this attachment), it also addresses the first.

IA. Large Molecule Studies: Two of the most important and fundamental scientific issues associated with SMM gas sensors are: (1) How large and complicated can molecules be and still be amenable to SMM analysis, and (2) what are strategies for maximizing the list of molecules?

The fundamental problem is that the usual SMM spectroscopic strategy depends upon the narrowness of Doppler broadened spectral lines to separate them from broader power variations due to standing waves, etc. Since the latter are typically 10% of the total power and often one seeks to observe spectral lines that have fractional absorptions of 10^{-7} there are six orders of magnitude in sensitivity at stake.

If spectral lines have begun to merge into spectral ‘features’ there are at least two approaches that can gain back some or all of these six orders of magnitude.

Cavity Strategies: The use of high Q-cavities: Here one regains the sharp spectral feature to measure in the context of a sharp cavity resonance, whose Q and amplitude are both modified by the molecular absorption. In fact, it is possible to observe with great sensitivity weak continuum

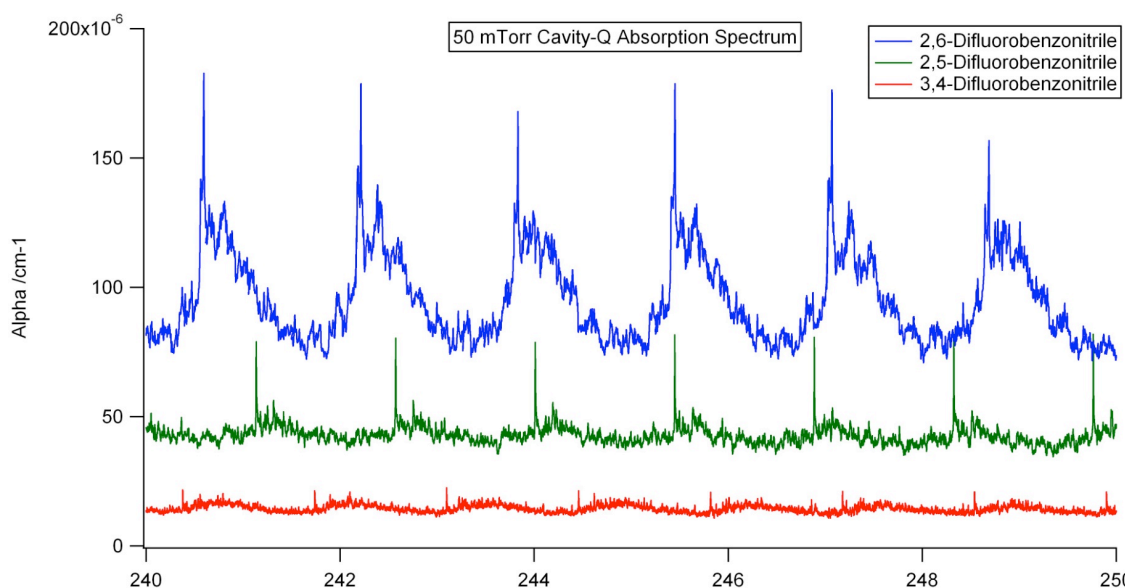


Figure 1. Cavity spectra of the difluorobenzonitriles.

contributions that are important in long path atmospheric transmission in the SMM [1, 2]. Figure 1 shows the cavity spectra of the difluorobenzonitriels. Although this is a highly compressed scale, it is possible to see individual lines (or at least close clumping of lines) in the red trace of the lightest of these species. However, as one goes to the heaviest, it can be seen that broader features emerge. It should also be noted that these cavity measurements measure *absolute* absorbance and the signal recovery does not depend upon narrow lines. Indeed, it can be seen that all three spectra have considerable continua component, as evidenced by their offset from zero. It should be noted that the heaviest species (shown in blue) should have the weakest lines, whereas its ‘features’ are actually the strongest. This results from the overlap of spectral lines, an effect that increases with molecular size. We have discussed this in some detail in an astrophysical context [3] and it can be a path both for astrophysics and terrestrial gas sensors towards the spectroscopic detection of larger species. The most important scientific question is the determination of where this overlap and blending of lines becomes so strong as to reduce the specificity of the remaining ‘features’ for the determination of the chemical composition of the mixture.

Stark Modulation Strategies: The sharp spectral features of Doppler limited SMM spectroscopy are ordinarily recovered by the imposition on the SMM carrier of a small FM modulation whose width is similar to the Doppler width of the line. An alternative is to apply a zero based Stark field that moves the frequency of the spectral line. Because ordinarily the frequency of the Stark shift is inversely proportional to the spectral frequency, this technique is usually used in low frequency (<40 GHz) microwave spectroscopy. However, it can be shown that in the THz virtually all large molecules have degeneracies that result in large Stark shifts. While this only applies to a subset of the total spectrum, for a sensor this is actually an advantage in that it results in a less crowded spectrum. Thus, for a sensor we gain two things: (1) the aforementioned reduction in spectral congestion, and (2) a modulation method that does not

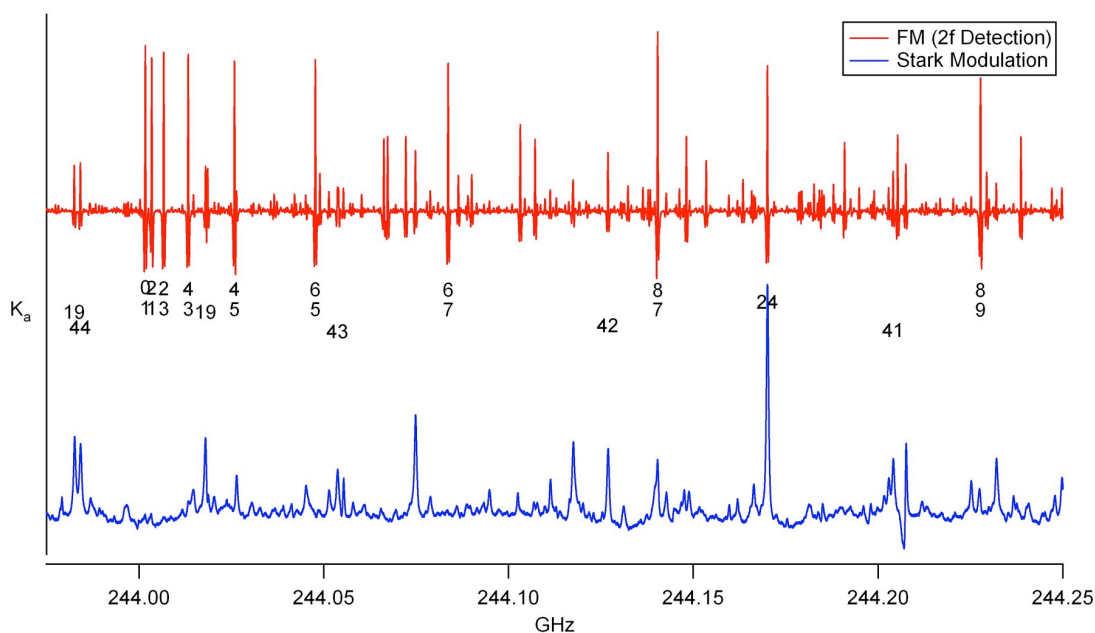


Figure 2. A comparison of and FM modulate spectrum and a Stark modulated spectrum.

depend upon narrow Doppler broadened lines. Figure 2 shows an example. An important research frontier for this approach is the determination of when the overlap from the frequency shifted Stark components begins to reduce the efficiency of the Stark modulation.

We have now obtained a considerable body of Stark data. We have also developed a theoretical model. The agreement between our data and the theory confirm our original thesis. Although Stark Modulation spectroscopy has been used almost exclusively at lower microwave frequencies because the Stark Effect in molecules is inversely proportional to the separation of states, we have noted that for large molecules that systematic degeneracies are formed at high J (the regime of SMM sensors) that provide very large Stark Modulation coefficients, even when averaged over the M_J degeneracy.

This work constituted the thesis work of David Graff who has just graduated with his Ph.D. It was done in the context of a combined general purpose Stark/Cavity system.

I.B: Diagnostics and process control in semiconductor wafer plasma reactors.

Although the processing of semiconductor wafers in plasma reactors is the basis of a number of multibillion-dollar organizations, these processes are more of an art form than a science. A major reason for this is that these plasmas are difficult to study and monitor by available means. On the other hand, a number of years ago we (with B.D. Guenther) considered the use of SMM spectroscopy for this application. Although we concluded that the physics of the application was nearly ideal, we did not pursue it because we felt that the SMM technology required was too specialized and unavailable for this to be a viable mass-market technology.

However, appropriate technology has become more available, and we were approached by a major supplier (Applied Materials) of semiconductor processing reactors with interest in this application. Briefly put, the low-pressure environment (10 – 100 mTorr) of these reactors is nearly ideal for SMM sensors, but several orders of magnitude below optimum for ‘optical’ sensors. Moreover, these plasmas are virtually noise free and 100% transparent in the SMM (a nice byproduct of the fact that it’s hard to produce radiation in the SMM by any method (including SMM plasma discharges)). Applied Materials supplied us with a list of molecules of interest, as well as the concentrations predicted by their simulations (they have no good means to measure these). This includes both small and large molecules. Spectra for an example of each

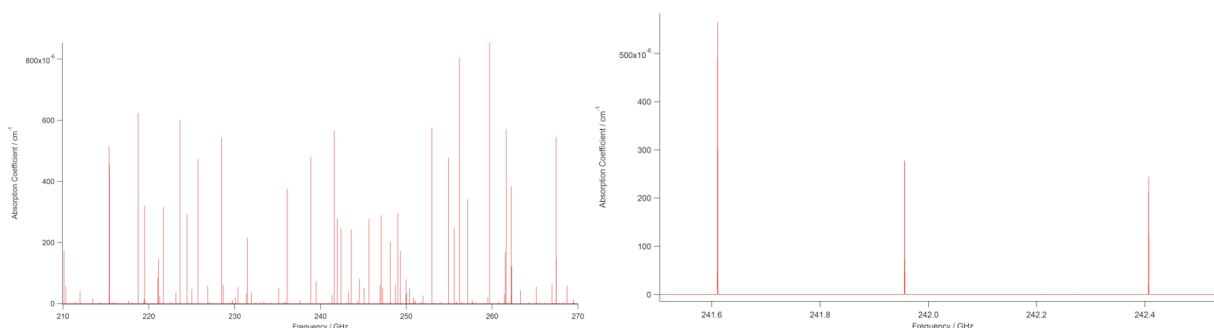


Figure 3. Spectrum of CH_2F_2 on a compressed (left) and expanded (right) scale.

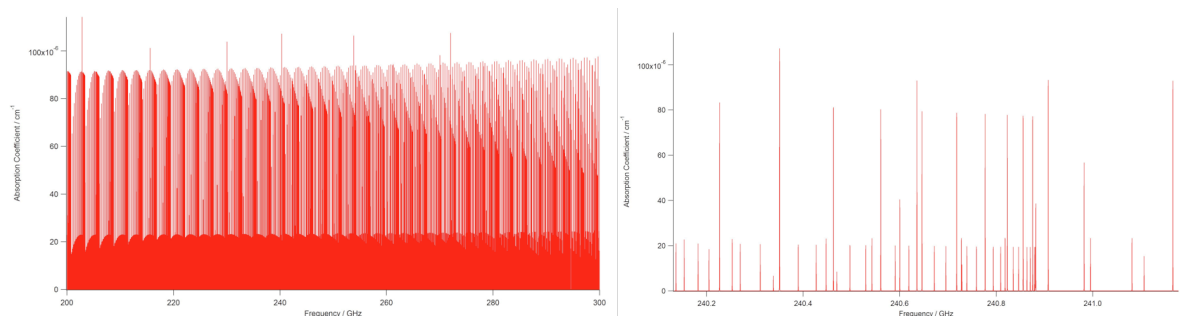


Figure 4. Spectrum of C_3F_4 on a compressed (left) and expanded (right) scale.

class are shown in Figs. 3 and 4. Because rotational spectroscopy is quantitative and theoretically well founded, it is possible to use simulations such as these, in combination with Applied Material's expected concentrations to determine the viability of the approach. The results are summarized in Table 1. This table shows that the majority of species of interest can be observed by a rather straightforward SMM spectrometer with large S/N and short (1 sec) integration times.

Another nice feature of this approach is that it can be applied to standard plasma reactors with little or no modification. Figure 5 shows a simple viewing geometry that is possible.

This geometry, along with a spectrometer of nominal sensitivity was used to calculate the S/N for the several species included in Table 1. It should be noted that while the ions have considerably lower S/N than the neutrals and radicals, it is not because ions are less favorable spectroscopically, but rather because there is a much smaller ion density in the plasma. It should also be noted that these S/N are for 1 sec of integration time and that much longer times are possible.

Table 1. Cross References for Detectability of Species of Interest

Molecule	Minimum (Simulation)	Minimum (analytical)	Mixture 1 (Sim: S/N)	Mixture 2 (Sim: S/N)	Mixture 3 (Sim: S/N)
CF_2	1.25×10^{10}	2.5×10^{10}	7.3×10^{12} (584)	9.1×10^{12} (728)	4.9×10^{12} (392)
CF	9×10^8	9.0×10^8	2.1×10^{11} (233)	1.2×10^{12} (1333)	3.3×10^{11} (367)
CF^+	6×10^8	5.0×10^8	1.0×10^8 (0.167)	1.9×10^9 (3)	
SF_2	4.4×10^9				1.5×10^{12} (340)
SF	6×10^8				1.4×10^{11} (233)
CF_3	2.2×10^{10}		1.1×10^{12} (50)	8.9×10^{12} (404)	
C_3F_4	1.75×10^{10}		7.3×10^{12} (417)		
CHF_3				2.4×10^{13}	
CH_2F_2	2.2×10^9				1.3×10^{13} (5909)

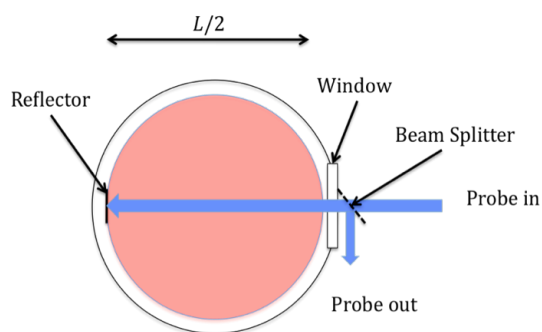


Figure 5 Simple sampling geometry for SMM probe of plasma reactor using existing windows.

Applied Materials has now provided us with a semiconductor plasma reactor for diagnostic and process control studies. This reactor is shown in Fig. 6. Figure 7 shows some results derived from this work. Work with this plasma reactor was very promising and we are now building a system for installation on their commercial scale reactors in Sunnyvale, CA. An abstract describing this work has been submitted to the upcoming 68th

International Symposium on Molecular Spectroscopy. Work on chemical sensors and process control (especially its implementation in low cost CMOS) is ongoing with sponsorship from the Semiconductor Research Corporation.



Figure 6. Plasma reactor provided by Applied Materials to OSU for proof of principle studies.

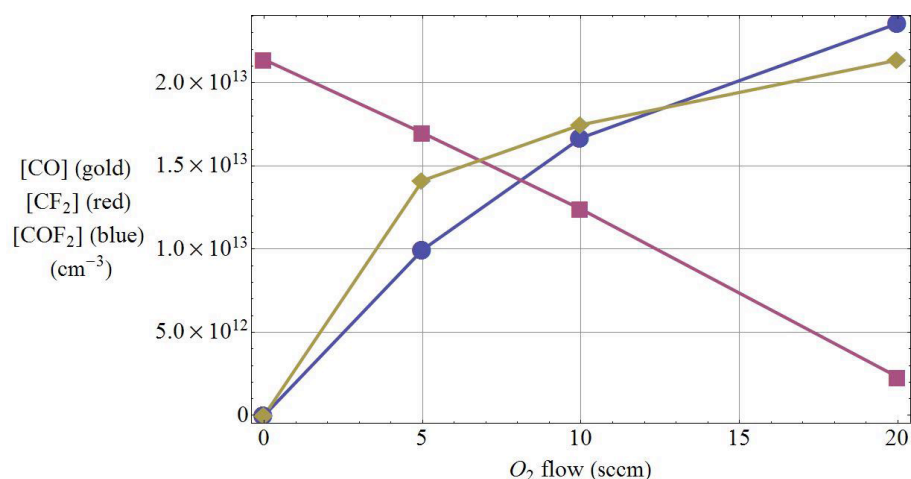


Figure 7. Measured absolute concentrations as a function of oxygen flow into a discharge of Ar and C₄F₈.

For some time we have made the general case that one of the attractive features of the SMM as a basis for gas sensors is the very small impact of atmospheric clutter. This is in stark contrast to the infrared where interfering clutter from species such as CO_2 and H_2O is often the limiting factor, rather than system sensitivity and resolution. Briefly put, CO_2 has no permanent dipole moment and thus no rotational spectrum in the SMM. H_2O has such a sparse spectrum in the SMM (at SMM resolution) as to have virtually no impact (in the region between 100 and 1000 GHz, it has about 10 lines that are ~ 0.001 GHz wide).

The magnitude of the difference between the SMM and IR is so great, that many found this general argument insufficient, so we did a detailed simulation and showed that even in unfavorable cases (a heavily polluted atmosphere and an unfavorable target gas), that the clutter limit for detection was less than 1 ppt. We had several interesting exchanges with referees on the way to the publication of this paper. Figure 4 shows one of these unfavorable cases [4].

On a more fundamental level, in collaboration with Brenda and Manfred Winnewisser we have been exploring the impact of quantum monodromy in large molecules. This work has attracted considerable attention and most recently a run at the Canadian Light Source [5, 6].

We have had considerable interactions with the outside world in relation to this work. Much of it has been related to the development of practical and affordable technology. For example, the plasma processing application mentioned above becomes much more attractive if the cost is

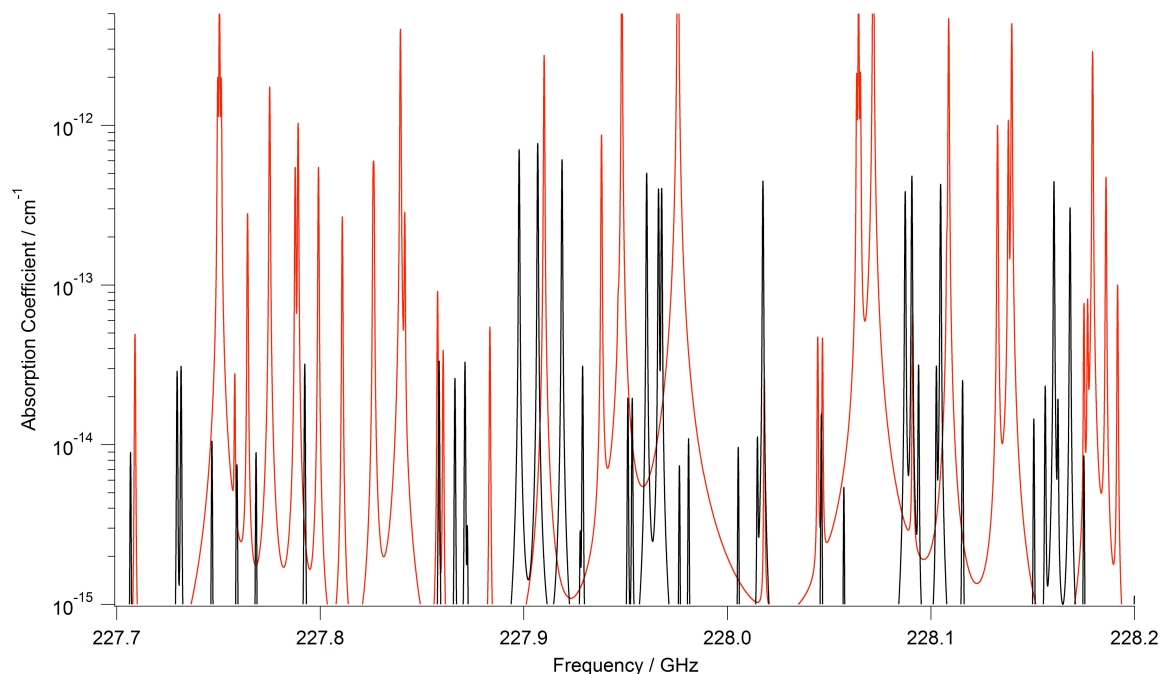
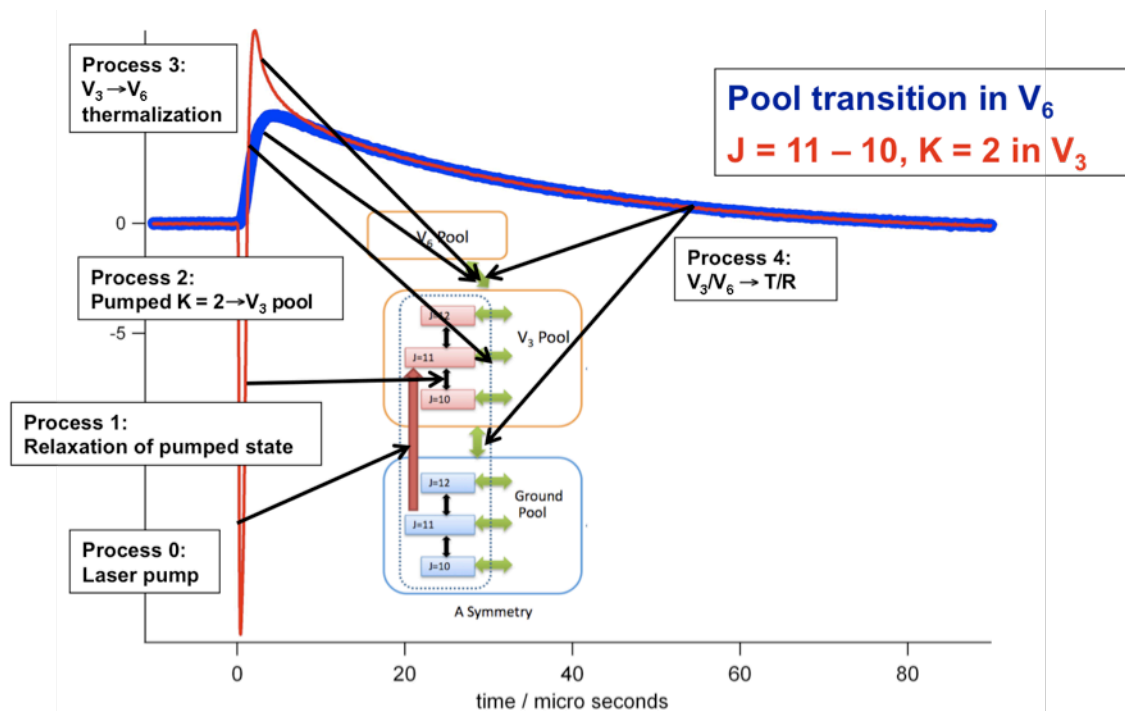


Figure 4. On a log scale, 1 ppt of Acrylonitrile (black) in the polluted troposphere (red). This figure includes a pressure broadening contribution that assumes a total pressure of 10 mTorr and a pressure broadening coefficient of 10 MHz/Torr. It can be seen that many of the lines of the target molecule extend several orders of magnitude above the background. For redundancy, many similar regions can be found.

lower than the current cost of our custom units. We have given seminars and had interactions with Texas Instrument (Kilby Labs – Dallas), IBM (Watson Research Laboratory – Yorktown Heights), Agilent (Santa Clara), and Semiconductor Research Corporation (TxACE – Dallas). In general these organizations are interested in the development of inexpensive CMOS circuitry and the development of market applications.

II. Infrared – SMM double resonance for atmospheric remote sensing: We are also explored the use of infrared – SMM double resonance as a basis for remote sensing at atmospheric pressure. Because of the rapid relaxation ($\sim 10^{-10}$ s) at atmospheric pressure and because of the resultant pressure broadening (~ 5 GHz), this is a much different and more challenging environment than the usual low-pressure regime of SMM spectroscopy. Very briefly put, in the double resonance approach the infrared pump laser is used to modulate the SMM signature, both to provide a means of separating the broad lines from the system baseline and to provide additional specificity to the sensor.

The underlying physics is the study of collisional energy transfer among the many states of the target molecule. This is done in the laboratory in the context of a double resonance pump probe experiment. A summary of some of the results are shown in Fig. 5, which also shows the relation of the observations to an energy transfer model. In these results, states directly pumped by the laser exhibit at short time large emission (down in the figure) signals. At later times the population moved by the pump is collisionally transferred to other rotational and vibrational



The arrows indicate the parts of the experimental time resolved data that contain information about the corresponding physical process

Figure 5. Experimental data of time resolved results and their relations to physical processes in the energy transfer model.

states. By tuning the frequency of the SMM probe, we can observe the different collisional processes.

A fundamental question for this double resonance approach is how common are overlaps between fixed laser pump frequencies and molecular absorptions. If they are rare, the approach will have little utility. From the closely related subject of low pressure Optically Pumped Far Infrared Lasers, we know that they are fairly rare at low pressure. However, we postulated that

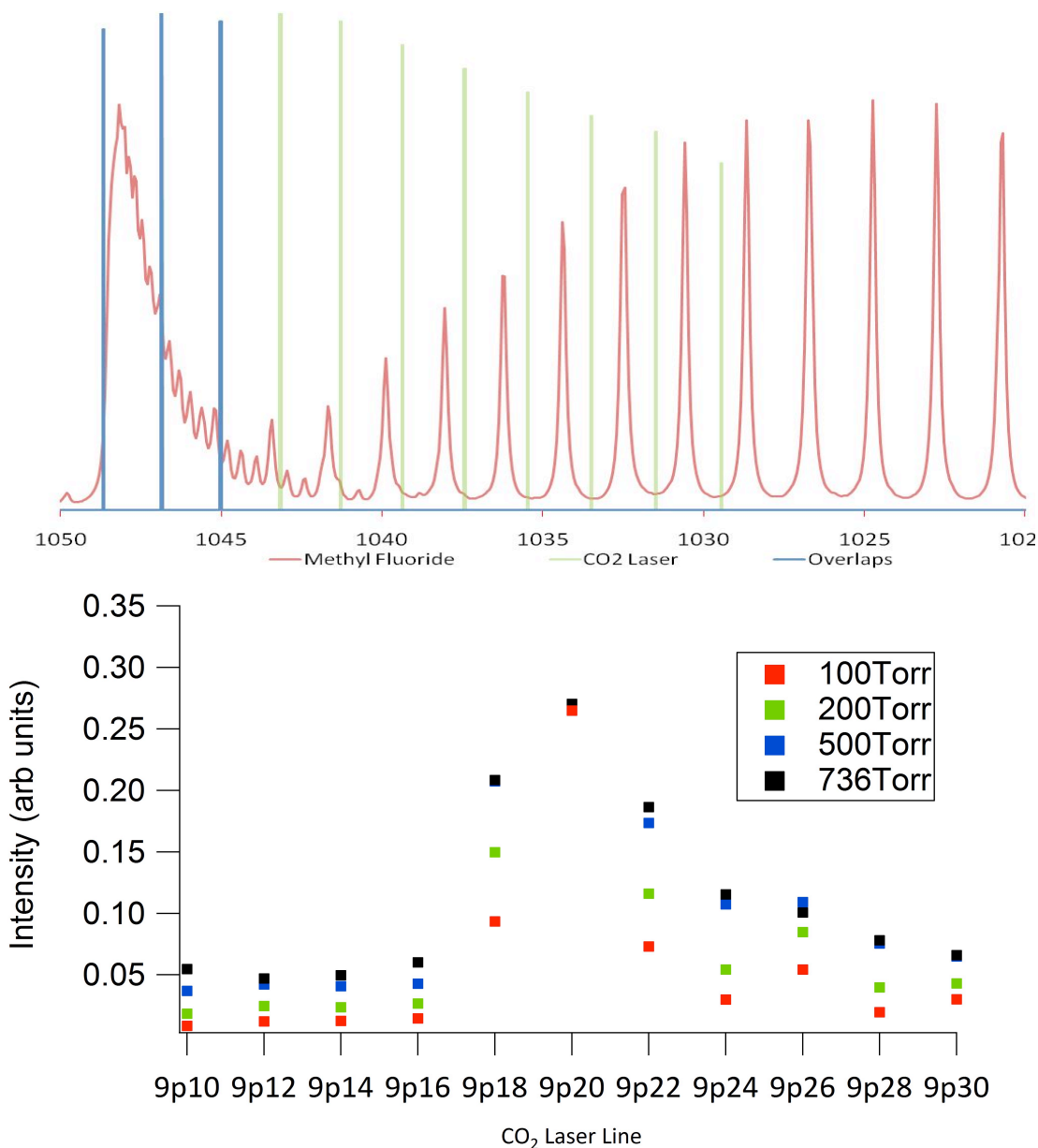


Figure 5a. Upper panel: Overlap between the laser pump frequencies (blue lines) and the atmospherically broadened lines of methyl fluoride. Lower panel: Experimental intensity of probe signal as a function of laser pump line and pressure. The middle blue line in the upper panel corresponds to the 9P20 line in the lower panel.

with the larger pressure broadened linewidths of atmospheric pressure that they would be fairly common. Figure 5a shows a confirmation of this expectation. In it a theoretical prediction (top panel, done by Dane Phillips and Henry Everitt of AMRDEC) is compared with our experimental observations shown in the lower panel [7]. As predicted, the off resonant pumps become more effective at higher pressure because of the increased linewidths.

For molecules of medium spectroscopic complexity (e. g. methyl fluoride or methyl chloride), spectroscopic knowledge is sufficient for a comparison between spectroscopic and collision theory and experiment.[8] Examples of experimental results for such species are shown in Figs. 6 and 7.

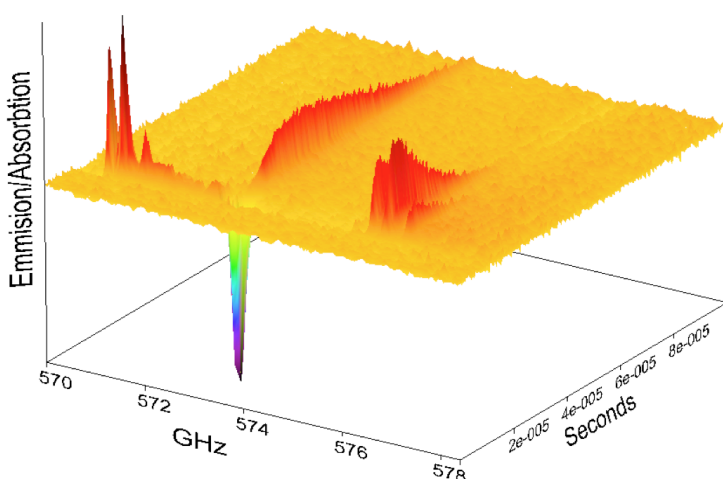


Figure 6. Double resonance signature of methyl chloride with the 9P14 CO₂ laser pump. Different signatures will result for each pump.

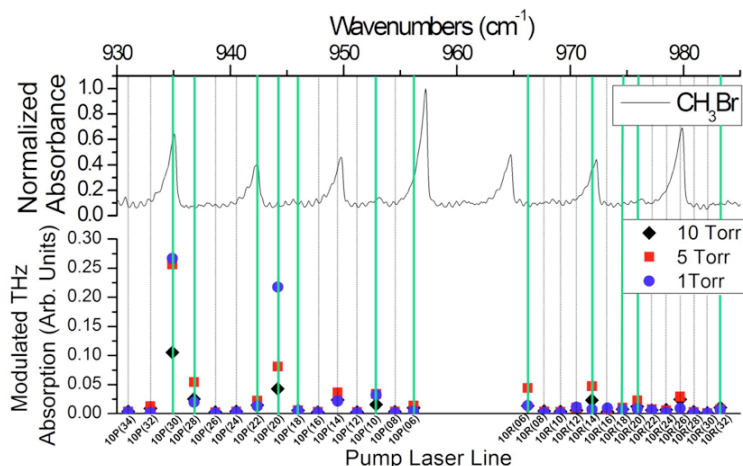


Figure 7. Impact of probe frequency on CH₃Br probe.

For these species it is also possible to use theory to study the overlap (a good thing because it adds to intensity) of probe lines in the double resonance mode. Figure 8 shows an overview of the results. Briefly, pumps of infrared stretching modes produce overlaps in the THz probes, but pumps of bending modes do not.

However, for larger molecules the theory is often unknown and direct experimental observations are required. An example, of the signature for a larger molecule 1,1,1 trifluoroethane is shown in Fig. 9.

If one considers the entire body of our experimental results and the aforementioned theory, it would appear that appropriate pump overlaps are common in large molecules and that unique THz probe signatures will result. We still need to do additional work to quantify how signal strengths scale

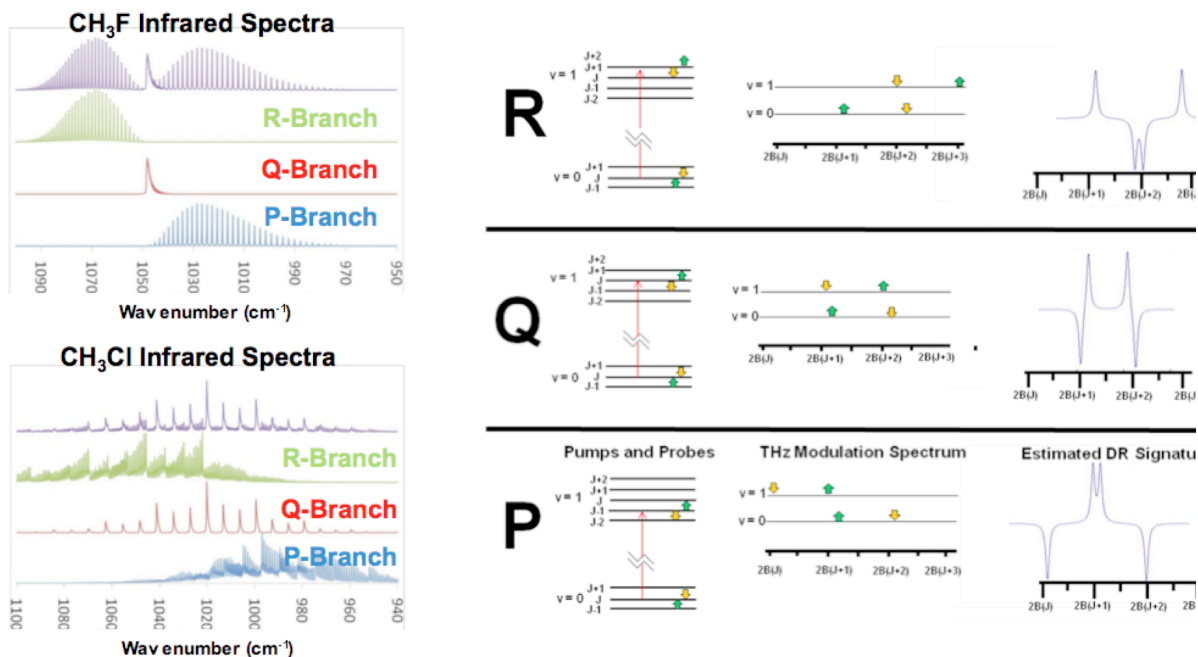


Figure 8. Theory for probe overlap as a function of vibrational type. For the pumped stretching mode in CH₃F, probes of the different K lines produce overlap, whereas for the pumped bending mode of CH₃Cl they do not.

with size.

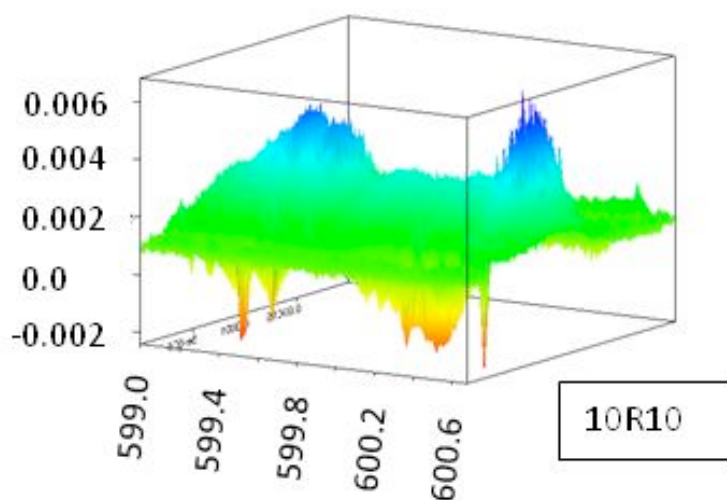


Figure 9. Double resonance signature of 1,1,1 trifluoroethane with the 10R10 CO₂ laser pump. Different signatures will result for each pump.

III. High Power Regime

Introduction: Science and technology in the submillimeter spectral region has been successfully carried out for many decades, but typically by identifying important problems that could be addressed with modest amount of power. However, there are important applications for which much larger amounts of power are required. As a result DARPA has a high power vacuum electronics program designed to address these needs. In parallel, we have been working to develop applications that these tubes will make possible. The two we report here are (1) the elimination of coherent speckle and the need for ‘special’ target orientation in active imaging and (2) a missile defense application for kill assessment.

III.A Active imaging

It has long been known that many SMM imaging applications require the sensitivity associated with active imaging. It has also been long known that coherent speckle severely degrades the image quality and recognition of active images. It is somewhat less well known that most demonstrations of detection of objects (from guns to trucks) take advantage of the strong specular reflections that occur when the target is strategically oriented perpendicularly to the sensing line of sight (the usual demonstration mode) [9].

During DARPA’s TIFT program, we proposed (and demonstrated at short range) a method based upon multiple mode illumination and the modulation of this illumination to eliminate both problems. For this work we used a 5 W EIK loaned to us by NRL and achieved elimination of coherent speckle and the need for special angles in the atrium of a large building. The results are shown in Fig. 10 [10]. This is a significant result because active imaging in this spectral region has been seriously limited by the speckle problem and the need to have targets cooperate to align

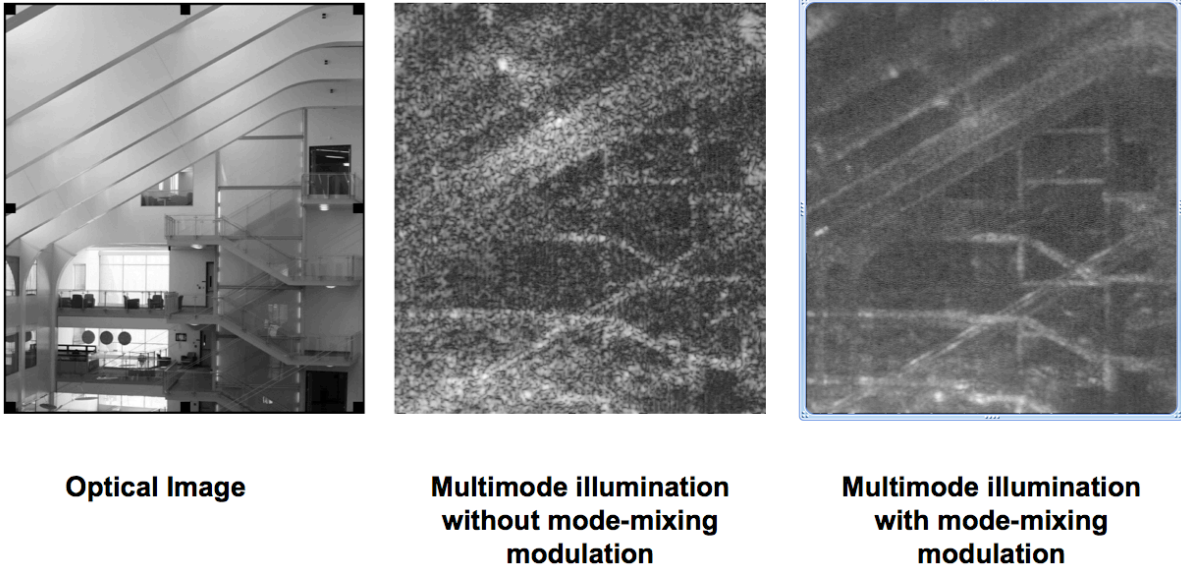


Figure 10. Optical image of the 50 m atrium of the Physics Research Building at OSU (left). Traditional active image of the atrium at 220 GHz, showing the dominance of coherent speckle (middle). Active image of the atrium with modulated mode mixing, showing the elimination of the coherent speckle (right).

themselves with the sensor.

During this project we also became involved in a STTR with a small business, IERUS, in Huntsville, AL. The topic was the calculation of radar cross sections of targets and clutter in the 90 – 300 GHz region. To first order this is an exercise in numerical modeling, which is not our expertise. However, at these higher frequencies surface roughness and the speckle that results become important. Our role was two fold: (1) To use our theoretical and experimental understanding of speckle in the millimeter-wave to provide statistical models that are appropriate for inclusion in numerical models and to consider tractable ways to describe the effects of surface roughness, and (2) to develop an experimental system to use for comparison of modeling to experiment. The most significant of these results is that we have shown that it is possible to model RCSs of rough surfaces, *without detailed knowledge of the roughness*, and have shown excellent agreement between our models and experiments.

This project led us to develop a chirped range sensitive system, a technology that we plan to incorporate into our 2-D imager to provide information about the third dimension in the imaging system discussed above. However, the NRL EIK tube that we used for these atrium experiments was unavailable to us (a combination of power supply problems and it being needed for other projects at NRL) until after the end of the no cost extension. As a point of information, when we did get the EIK from NRL we were able to make range resolved, speckle free images of the entire atrium, build a theory of how this works, and obtain the results that provided the basis for a PhD thesis.

III.B Spectroscopic remote sensing

Above we discussed the use of a double resonance scheme to overcome the problems of both specificity and sensitivity in chemical remote sensing near the surface of the earth that are induced by the large pressure broadened linewidths of the target chemicals. Here we will simply note that in our analyses of this problem a relatively high power broadband probe system is required (unless one has cooperative retro-reflectors) for ranges of ~ 1 km.

More recently we have become involved with a different problem, but one with similar broadband, high power probe requirements. We (along with a small business, Applied Quantum Technologies) were encouraged to consider an SBIR issued by MDA that proposed to use submillimeter techniques for missile intercept kill analysis at relatively late times. Briefly put, the general idea was that because the intercept cloud cools rapidly, the thermal emission that is ordinarily observed in the optical or IR ends before a cooler, lower pressure regime that is potentially rich in highly specific signatures begins.

In our Phase 1 study, we considered this problem in some detail and found that there were reasonable prospects that this general concept would stand up to a more detailed analysis. We were awarded a Phase 2 SBIR to study this. Figure 11 shows the one of the results of our Phase 1 calculations of the spectroscopic interaction of UO with the submillimeter probe and Fig. 12 convolves this result with system parameters for a simulation of sensor sensitivity.

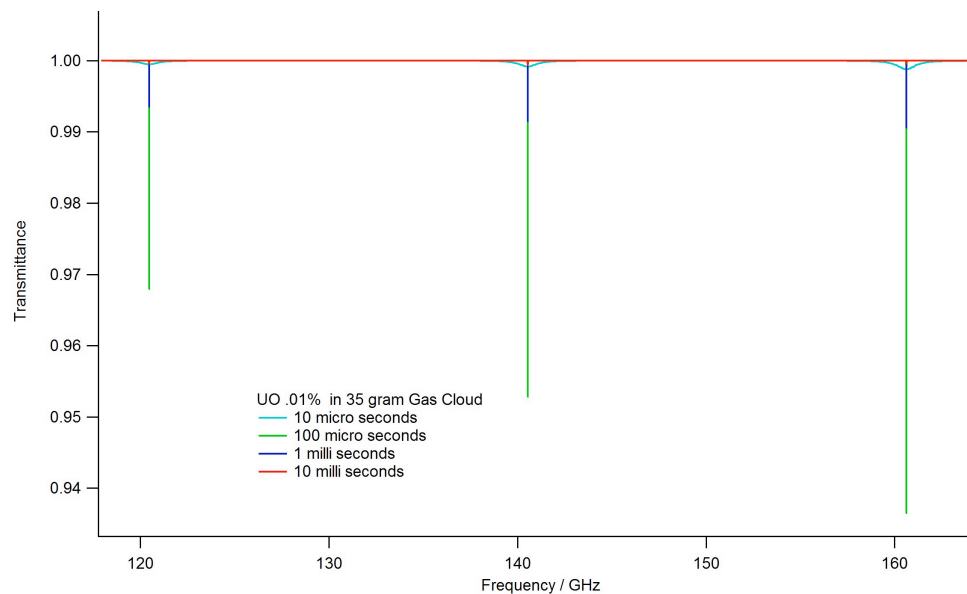


Figure 11. Transmission spectrum of a 0.01% sample of uranium oxide in 35 grams total along the central cord of the expanding gas cloud.

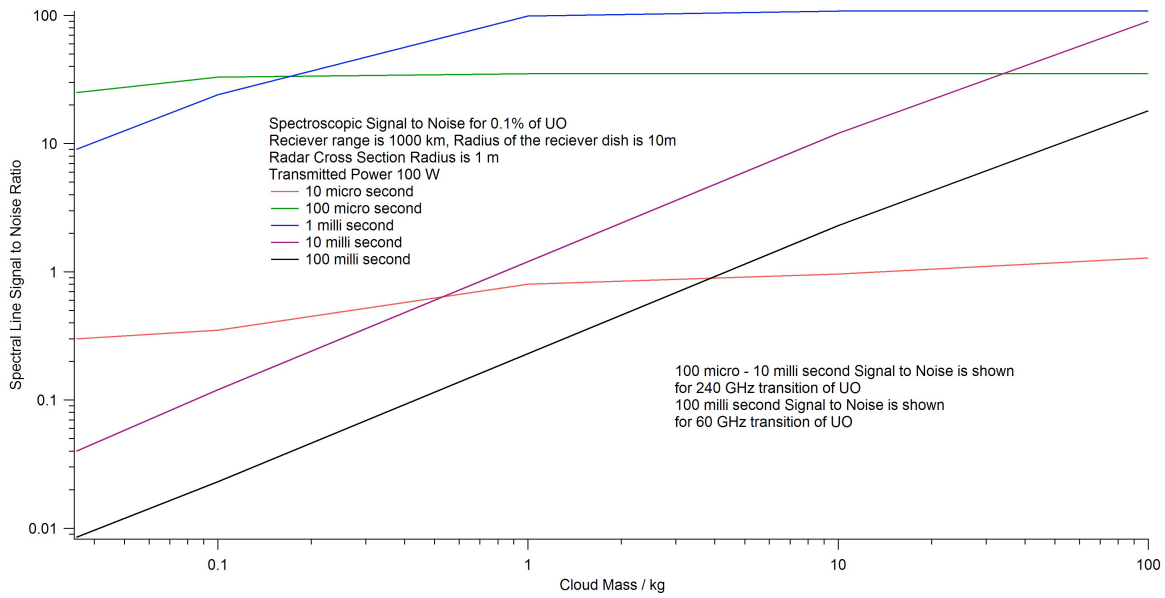


Figure 12. System spectroscopic S/N for 0.1% concentration of UO for 100 W probe, 10 m antenna at 1000 km as a function of total mass and time.

In Phase II our results were convolved with model results from SSI to predict the UO signature. Results are shown in Fig. 13. The strength and specificity (there are similar examples for many more lines) support the proposition that it is possible to develop important sensors for MDA in the submillimeter.

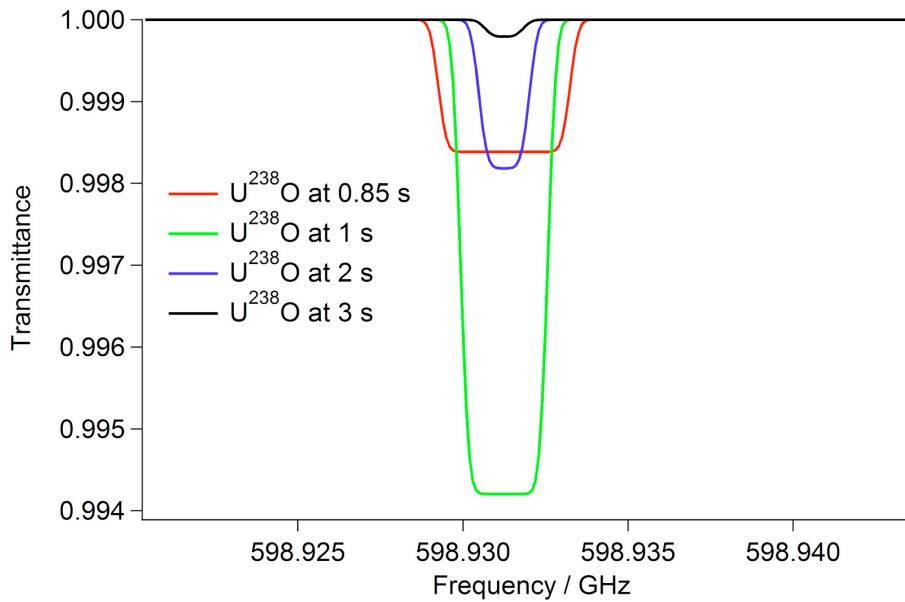


Figure 13. Fractional transmission of a probe signal through a model intercept cloud.

- [1] A. Meshkov and F. C. De Lucia, "Laboratory Measurements of Dry Air Atmospheric Absorption with a Millimeter Wave Cavity Ringdown Spectrometer," *Journal of Quantitative Spectroscopy and Radiative Transfer*, vol. 108, pp. 256-276, 2007.
- [2] A. I. Meshkov and F. C. De Lucia, "Broadband absolute absorption measurements of atmospheric continua with millimeter wave cavity ringdown spectroscopy," *Rev. Sci. Instr.*, vol. 76, pp. 083103-1/10, 2005.
- [3] I. R. Medvedev and F. C. De Lucia, "An Experimental Approach to the Prediction of Complete Millimeter and Submillimeter Spectra at Astrophysical Temperatures: Applications to Confusion-limited Astrophysical Observations," *Astrophys. J.*, vol. 656, pp. 621-628, 2007.
- [4] I. R. Medvedev, C. F. Neese, G. M. Plummer, and F. C. De Lucia, "Impact of Atmospheric Clutter on Doppler-limited Gas Sensors in the Submillimeter/Terahertz," *Applied Optics*, vol. 50, pp. 3028-3042, 2011.
- [5] B. P. Winnewisser, M. Winnewisser, I. Medvedev, M. Behnke, F. C. De Lucia, S. C. Ross, and J. Koput, "Experimental Confirmation of Quantum Monodromy: The Millimeter Wave Spectrum of Cyanogen Isothiocyanate NCNCS," *Phys. Rev. Lett.*, vol. 95, pp. 243002-243006, 2005.
- [6] B. P. Winnewisser, M. Winnewisser, I. R. Medvedev, F. C. De Lucia, S. C. Ross, and J. Koput, "Analysis of the FASSST Rotational Spectrum of NCNCS in View of Quantum Monodromy," *J. Phys. Chem. Chem. Phys.*, vol. 12, pp. 8158-8189, 2010.
- [7] D. J. Phillips, E. A. Tanner, H. O. Everitt, I. R. Medvedev, C. F. Neese, J. Holt, and F. C. De Lucia, "Infrared/Terahertz Double Resonance for Chemical Remote Sensing: Signatures and Performance Predictions " in *SPIE Conference on Terahertz Physics, Devices, and Systems IV - Advanced Applications in Industry and Defense*, Orlando, FL, 2010, p. 76710F.
- [8] D. J. Phillips, E. A. Tanner, F. C. De Lucia, and H. O. Everitt, "Infrared-terahertz double-resonance spectroscopy of CH₃F and CH₃Cl at atmospheric pressure," *Phys. Rev. A.*, vol. 85, pp. 052507/1-13, 2012.
- [9] D. T. Petkie, J. A. Holt, M. A. Patrick, and F. C. De Lucia, "Multimode illumination in the terahertz for elimination of target orientation requirements and minimization of coherent effects in active imaging systems," *Opt. Eng.*, vol. 51, pp. 091604-1,7, 2012.
- [10] M. A. Patrick, J. A. Holt, C. D. Joye, and F. C. De Lucia, "Elimination of Speckle and Target Orientation Requirements in Millimeter-wave Active Imaging by Modulated Multimode Mixing Illumination," *J. Opt. Soc. Am. A*, vol. 29, pp. 2643-2656, 2012.

Tech Transfer – Interactions - Industry

Texas Instruments/Semiconductor Research Corporation: We were contacted by the Semiconductor Research Corporation and organizations associated with it (Texas Instruments and the University of Texas, Dallas) who have interest in gas sensor applications for the mass market. Staff from both organizations have visited us and we have given seminars at TI, SRC, and at SRC organized events. TI is especially interested in exploring if low cost and low power CMOS technology can be used in our application. They have made a significant commitment in both personnel and capital funds to set up a SMM/THz laboratory as a part of this joint work. We are working closely to help them do this.

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Applied Materials (a member of the Semiconductor Research Corporation): Applied Materials learned of our gas sensor work from one of our SRC Electronic Seminars. They were interested if the SMM/THz sensor might be a good tool for diagnostics and process control in their semiconductor plasma processing reactors. It turns out that this is a very good application for SMM/THz sensors and that we had, in fact, considered it about twenty years ago (As an aside, much of the basic work that shows that this is possible is contained in the theses of Dave Skatrud and Bill Clark). We did not pursue it at that time because we felt that the technology was too immature for this to be a practical industrial tool. The technological maturity represented by our gas sensor has changed this. We are now in detailed discussions with them to find a ‘path forward’. This includes our spectroscopic simulations based on their calculations (there are few reliable measurements) of species concentrations that show many species of interest that are clearly quantitatively observable. Many of these are small molecules for which we know the spectroscopy well, but some are larger molecules for which the techniques we are developing will be important. AM is designing a semiconductor plasma reactor for us, which can be mated with one of our systems for a demonstration. This reactor was delivered and Proof of Principle demonstrations successful. We are now finishing a system for delivery to AM in Sunnyvale, CA for tests with their commercial scale reactors.

Contact: Phillip Stout (Phillip_Stout@amat.com)

IBM/TI/AM have supported our proposal to the Semiconductor Research Corporation for a ‘Long Horizons’ grant, which was awarded. In addition to extension of the aforementioned work, we have proposed and begun to build a generalized ‘end-to-end’ model that considers the parameters and characteristics of THz systems in the context of proposed applications. It is being designed for engineers (who are generally not knowledgeable of the phenomenology of targets) to use to see the impact and significance of design choices they might make. As example applications we will use the two listed above, along with the imaging applications discussed in this report.

Contact: Alberto Valdes (avaldes@us.ibm.com)

Northrup-Grumman: Ken Ewing (of NRL – see below) has developed an interest in our sensor work and put us in contact with Northrup-Grumman. Three staff from NG visited us for some detailed technical discussions. Their application is with an unnamed customer that we infer is a part of the intelligence community. This interaction is potentially interesting, but without more a more detailed understanding of the requirement it is difficult to say if it will be an appropriate problem. That said, the general category of airborne chemical intelligence has always been one of the applications that is technically attractive. NG was unable to secure funding for this project and it has ended.

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Imperium: Imperium is a manufacturer of ultrasonic imaging devices. They contacted us because of their interest in whether or not their ultrasonic array might also be a useful array for a THz imager. Interestingly, the PZT material that they use in their ~100 x 100 array, is also a pyroelectric material that is a well known THz detector. While parameters (e. g. thermal time constant) that are important for this application are unknown, our preliminary analysis showed that it would appear that in most remote SMM/THz imaging application the sensitivity of a

pyroelectric device would be too low, there may be a heterodyne operation mode that would use some of the new high power tubes being developed by DARPA/MTO as a local oscillator. This project has ended.

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Bob Lasser (blasser@imperiuminc.com)

Applied Quantum Technologies: In the main body of this report we have described a collaboration with a small business, Applied Quantum Technologies, in the context of an MDA SBIR. Phase 1 and Phase 2 were successfully completed. During Phase 2 we gave a presentation at an MDA review that attracted considerable interest and were encouraged by MDA to prepare a proposal to proceed via the design and construction of a THz system that could be used both for lab and chamber experiments and which also could serve as a prototype for fieldable systems. Unfortunately, the proposed work was outside of the scope of the SBIR announcement that was released and the proposal was not funded.

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Robert Lontz (rlontz@appliedquantumtechnologies.com)

Tech Transfer – Interactions – DoD

AMRDEC: We have close contacts and joint projects with AMRDEC. In addition to those most directly related to this project, Dr. Everitt has had extensive interaction with potential customers. This interest focuses most on point and remote gas sensors and SMM/THz imagers. These include TRADOC and MSCOE (Ft. Lenora Wood), and ERDEC (Edgewood), as well as offices within AMRDEC (Redstone).

Contact: Henry Everitt (henry.everitt@amrdec.army.mil)

NRL: Ken Ewing of NRL is setting up an in-house SMM/THz program and we have exchanged several visits. In addition to the Northrup-Grumman interaction discussed above, he is interested in a field trial of our gas sensor in the Pentagon and is in discussions with them about paths for doing so. We are working to resolve the first issue: that Phase 1 of the MACS program did not leave us with a 'loner' unit, appropriate for unattended use.

Contact: Ken Ewing (ken.ewing@nrl.navy.mil)

There is a separate interaction that involves the vacuum electronics group at NRL. This is the project listed below under DARPA.

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John Pasour (john.pasour@nrl.navy.mil)

DARPA: The DARPA HiFIVE tube program will result in broadband tubes which will fundamentally alter the way we can approach several applications of interest to us, most notably imaging and remote gas sensing. DARPA has added funds to this contract for a start of such a program. NRL is also actively involved and has provided us with an EIK, which we have used to make coherent speckle free images on the scale of a large atrium

Contact: John Albrecht (John.Albrecht@darpa.mil)