

# Segmented chirped-pulse Fourier transform submillimeter spectroscopy for broadband gas analysis

Justin L. Neill,<sup>1</sup> Brent J. Harris,<sup>2</sup> Amanda L. Steber,<sup>2</sup> Kevin O. Douglass,<sup>3</sup>  
David F. Plusquellic,<sup>3</sup> and Brooks H. Pate<sup>2,\*</sup>

<sup>1</sup>Department of Astronomy, University of Michigan, 500 Church St., Ann Arbor, MI 48109, USA

<sup>2</sup>Department of Chemistry, University of Virginia, Chemistry Building, Charlottesville, VA 22904, USA

<sup>3</sup>National Institute of Standards and Technology, 325 Broadway Ave, Boulder, CO 80305, USA

\*brookspate@virginia.edu

**Abstract:** Chirped-pulse Fourier transform spectroscopy has recently been extended to millimeter wave spectroscopy as a technique for the characterization of room-temperature gas samples. Here we present a variation of this technique that significantly reduces the technical requirements on high-speed digital electronics and the data throughput, with no reduction in the broadband spectral coverage and no increase in the time required to reach a given sensitivity level. This method takes advantage of the frequency agility of arbitrary waveform generators by utilizing a series of low-bandwidth chirped excitation pulses paired in time with a series of offset single frequency local oscillators, which are used to detect the molecular free induction decay signals in a heterodyne receiver. A demonstration of this technique is presented in which a 67 GHz bandwidth spectrum of methanol (spanning from 792 to 859 GHz) is acquired in 58  $\mu$ s.

© 2007 Optical Society of America

**OCIS codes:** (120.6200) Spectrometers and spectroscopic instrumentation; (040.6070) Solid state detectors; (300.6240) Spectroscopy, coherent transient; (300.6495) Spectroscopy, terahertz; (300.6310) Spectroscopy, heterodyne.

---

## References and links

1. W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (John Wiley and Sons, 1984).
2. C. Townes and A. Schawlow, *Microwave Spectroscopy* (Dover, 1975).
3. D. Petkie, T. Goyette, R. Bettens, S. Belov, S. Belov, S. Albert, P. Helminger, and F. De Lucia, "A fast scan submillimeter spectroscopic technique," *Rev. Sci. Instrum.* **68**(4), 1675–1683 (1997).
4. I. R. Medvedev, C. F. Neese, G. M. Plummer, and F. C. De Lucia, "Submillimeter spectroscopy for chemical analysis with absolute specificity," *Opt. Lett.* **35**(10), 1533–1535 (2010).
5. C. Neese, I. Medvedev, G. Plummer, A. Frank, C. Ball, and F. De Lucia, "Compact submillimeter/terahertz gas sensor with efficient gas collection, preconcentration, and ppt sensitivity," *IEEE Sens. J.* **12**(8), 2565–2574 (2012).
6. C. P. Endres, F. Lewen, T. F. Giesen, S. Schlemmer, D. G. Paveliev, Y. I. Koschurinov, V. M. Ustinov, and A. E. Zhucov, "Application of superlattice multipliers for high-resolution terahertz spectroscopy," *Rev. Sci. Instrum.* **78**(4), 043106 (2007).
7. M. H. Ordu, H. S. P. Muller, A. Walters, M. Nunez, F. Lewen, A. Belloche, K. M. Menten, S. Schlemmer, "The quest for complex molecules in space: laboratory spectroscopy of n-butyl cyanide, n-C<sub>4</sub>H<sub>9</sub>CN, in the millimeter wave region and its astronomical search in Sagittarius B2(N)," *Astron. Astrophys.* **541**, A121 (2012).
8. R. A. Motiyenko, L. Margules, E. A. Alekseev, J.-C. Guillemin, J. Demaison, "Centrifugal distortion analysis of the rotational spectrum of aziridine: Comparison of different Hamiltonians," *Astron. Astrophys.* **264**, 94–99 (2010).
9. A. Krupnov, M. Tretyakov, Y. Dryagin, and S. Volokhov, "Extension of the range of microwave spectroscopy to 1.3 THz," *J. Mol Spectrosc.* **170**(Spec.), 279–284 (1995).
10. B. Drouin, F. Maiwald, and J. Pearson, "Application of cascaded frequency multiplication to molecular spectroscopy," *Rev. Sci. Instrum.* **76**(9), 093113 (2005).
11. V. B. Podobedov, D. F. Plusquellic, and G. T. Fraser, "THz Laser Study of Self-Pressure and Temperature Broadening and Shifts of Water Lines for Pressures up to 1.4 kPa," *J. Quant. Spectrosc. Radiat. Transf.* **87**(3-4), 377–385 (2004).

12. G. G. Brown, B. C. Dian, K. O. Douglass, S. M. Geyer, S. T. Shipman, and B. H. Pate, "A broadband Fourier transform microwave spectrometer based on chirped pulse excitation," *Rev. Sci. Instrum.* **79**(5), 053103 (2008).
13. D. Zaleski, J. Neill, M. Muckle, N. Seifert, P. Carroll, S. Wicidius Weaver, and B. Pate, "A Ka-band chirped-pulse Fourier transform microwave spectrometer," *J. Mol. Spectrosc.* **280**, 68–76 (2012).
14. G. B. Park, A. H. Steeves, K. Kuyanov-Prozument, J. L. Neill, and R. W. Field, "Design and evaluation of a pulsed-jet chirped-pulse millimeter-wave spectrometer for the 70–102 GHz region," *J. Chem. Phys.* **135**(2), 024202 (2011).
15. E. Gerecht, K. O. Douglass, and D. F. Plusquellic, "Chirped-pulse terahertz spectroscopy for broadband trace gas sensing," *Opt. Express* **19**(9), 8973–8984 (2011).
16. A. Steber, B. Harris, J. Neill, and B. Pate, "An arbitrary waveform generator based chirped pulse Fourier transform spectrometer operating from 260 to 295 GHz," *J. Mol. Spectrosc.* **280**, 3–10 (2012).
17. T. Crowe, W. Bishop, D. Porterfield, J. Hesler, and R. Weikle, "Opening the terahertz window with integrated diode circuits," *IEEE J. Solid-State Circuits* **40**(10), 2104–2110 (2005).
18. Certain equipment or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply endorsement or that the equipment identified is the best available.
19. J. U. White, "Long optical path of large aperture," *J. Opt. Soc. Am.* **32**(5), 285–288 (1942).
20. R. G. Pilston and J. U. White, "A long path gas absorption cell," *J. Opt. Soc. Am.* **44**(7), 572–573 (1954).
21. V. B. Podobedov, D. F. Plusquellic, and G. T. Fraser, "Investigation of the water-vapor continuum in the THz region using a multipass cell," *J. Quant. Spectrosc. Radiat. Transf.* **91**(3), 287–295 (2005).
22. H. M. Pickett, R. L. Poynter, E. A. Cohen, M. L. Delitsky, J. C. Pearson, and H. S. P. Muller, "Submillimeter, millimeter, and microwave spectral line catalog," *J. Quant. Spectrosc. Radiat. Transf.* **60**(5), 883–890 (1998).
23. J. McGurk, T. Schmalz, and W. Flygare, "Fast passage in rotational spectroscopy: theory and experiment," *J. Chem. Phys.* **60**(11), 4181 (1974).
24. S. M. Fortman, I. R. Medvedev, C. F. Neese, and F. C. De Lucia, "How complete are astrophysical catalogs for the millimeter and submillimeter spectral region?" *Astrophys. J.* **725**(1), L11–L14 (2010).

## 1. Introduction

The (0.2 to 1) THz spectral region is well-suited for room-temperature gas mixture analysis by molecular rotational spectroscopy. Gas-phase species with a permanent dipole moment have unique rotational spectral signatures due to the relationship between the rotational spectrum, expressed to first order through the three-dimensional moments of inertia, and the molecular structure [1,2]. At room temperature, the Boltzmann distribution-governed spectrum peaks at submillimeter wavelengths for most volatile molecules, and the high resolving power of rotational spectroscopy ( $R \sim 10^6$ ) has motivated the development of a number of spectrometer designs for this region [3–11]. In particular, advances in digital technology in recent years have enabled the development of broadband techniques to rapidly characterize gas mixtures for a number of applications.

One instrumental method in this area that takes advantage of recent technological advances is chirped-pulse Fourier transform (CP-FT) spectroscopy, which was first designed for the microwave spectral region [12,13] and has more recently been shown to have significant promise for millimeter and submillimeter spectroscopy. CP-FT has been demonstrated to be capable of measuring 10–30 GHz of spectral bandwidth in a few microseconds [14–16]. In these experiments, a short ( $\ll T_2$ ) chirped excitation pulse (linear frequency sweep) is applied to a gas sample. After the excitation pulse is turned off, molecules continue to emit radiation at their characteristic spectral frequencies (the free induction decay (FID) signal). These signals are downconverted, amplified, and digitized, after which, the broadband molecular spectrum in the frequency domain is obtained by fast Fourier transformation. CP-FT spectroscopy in the microwave was made possible by the development of high-bandwidth arbitrary waveform generators (AWGs) as well as high-bandwidth digital oscilloscopes.

The sensitivity of CP-FT spectroscopy at microwave frequencies [12,13] is due, in part, to the availability of high power (approximately 300 W peak power) broadband pulsed amplifiers. For application to submillimeter spectroscopy, a critical technological advance for sample excitation was the development of high-power, high-bandwidth active multiplier chains (AMCs); a great deal of the impetus behind the development of broadband AMCs has come from the radio astronomy community in the construction of high-bandwidth telescopes

operating in this frequency region, such as the Atacama Large Millimeter/submillimeter Array (ALMA) [17]. AMCs can have typical bandwidths of 10-20% of the center frequency of the device, which can correspond to bandwidths of 50-100 GHz. For the implementations of millimeter/submillimeter CP-FT spectroscopy that have been previously described [14–16], the entire measurement bandwidth is addressed by a single chirped pulse, and the molecular response (FID) is downconverted by a single-frequency local oscillator (LO) and digitized. Therefore, the bandwidth that can be addressed in a single measurement is limited by the capabilities of the digital oscilloscope. While the highest commercially available oscilloscope bandwidth continues to improve (the current state of the art is a 160 GS/s oscilloscope with 63 GHz hardware bandwidth [16]), digitization of the full spectral bandwidth may not be practical, due to the high cost involved and massive data throughput requirements, leading to significant data management overhead.

In this manuscript, we present a technique, which we call segmented chirped-pulse Fourier transform spectroscopy, that offers a cost- and time-efficient alternative to the previously reported CP-FT techniques. Particularly for static gas samples where there is no sample recovery time, techniques that approach a 100% measurement duty cycle are desired. The segmented CP-FT method takes advantage of the frequency agility of the arbitrary waveform generator (AWG) to measure the spectrum in many small segments, but without any increase in the data acquisition time required to reach a given sensitivity level and with a significant reduction in the digitizer sampling requirements. This has the effect of increasing the effectiveness of submillimeter chirped pulse spectroscopy for static gas samples while lowering instrumental cost.

## 2. Experimental

A schematic of the segmented chirped-pulse Fourier transform instrument is presented in Fig. 1. A 12 GS/s dual channel AWG (Tektronix AWG8000 series [18]) was used as the source for both the chirped excitation pulse and the heterodyne detector LO. One AWG channel is used to generate a series of 232 chirped pulses, each 25 ns in duration, 4 MHz in bandwidth, and sequentially addressing the frequency range from 2000 to 2928 MHz. The frequency range of the pulses from the AWG is chosen so that harmonic content of the AWG can be filtered prior to input to the AMCs. Following each chirped pulse, there is a 225 ns time period for signal detection, making the total length of each segment 250 ns. The second AWG channel generates a train of 232 different single-frequency sine waves, synchronized in time to the chirped pulses and each offset 60 MHz above the corresponding chirp. A conceptual spectrogram of the two AWG waveforms is found in Fig. 2.

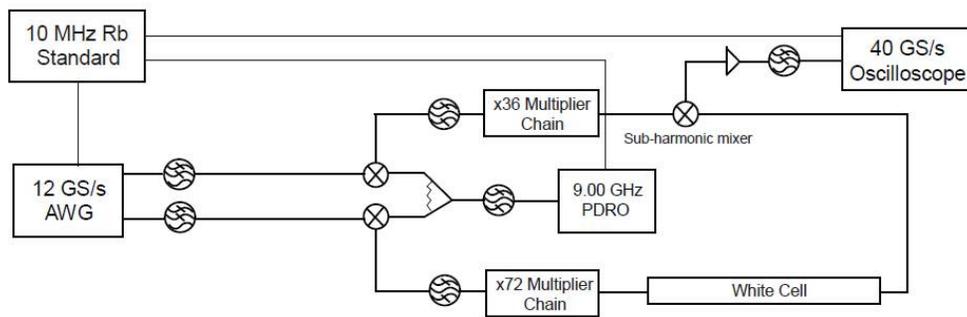


Fig. 1. A schematic of the segmented CP-FT submillimeter-wave spectrometer used for this study. For more information, see the text and [15].

The outputs of both AWG channels are upconverted in two double-sideband mixers by the divided output of a 9.00 GHz phase-locked dielectric resonant oscillator (PDRO, Microwave

Dynamics PLO-4000-9.0), and the upper sidebands of this mixing stage are selected by bandpass filters. The chirped pulses are then input to a  $\times 72$  AMC with a mid-band power output of approximately  $300 \mu\text{W}$ . After multiplication, each chirped pulse has a bandwidth of 288 MHz. The output is then broadcast into a 25 m pathlength White cell [19–21] loaded with 40 mTorr of methanol. The radiation is coupled into and out of the White cell using Teflon windows, lenses and off-axis parabolic mirrors. Emission from the chamber is fed into a sub-harmonic mixer (SHM) where the LO is the second AWG waveform, multiplied by a  $\times 36$  AMC. The IF output of the mixer, which for each segment spans 4032–4320 MHz, was amplified by a low-noise cw amplifier (Miteq AFS5-00100800-14-10P-5) and then digitized on a 40 GS/s digital oscilloscope (LeCroy 8zi [18]). Frequency calibration and phase stability are achieved by locking the PDRO, AWG, and oscilloscope to a common 10 MHz Rb frequency standard. The digitized data trace of the entire segmented time domain is acquired with a single oscilloscope trigger (the waveform is well within the record length limit of the oscilloscope) and processed by extracting a 100 ns portion of the FID of each segment, beginning 30 ns after the end of the excitation pulse (to allow for amplifier recovery), applying a Kaiser-Bessel window function for side-lobe suppression, and Fourier transforming the result. The LO frequency is then added to each segment to reconstruct the molecular frequency axis, and the segments are concatenated.

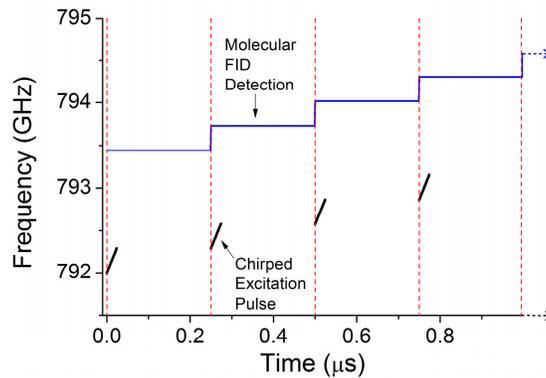


Fig. 2. Conceptual segmented CP-FT spectrogram of the two AWG waveforms upconverted and multiplied to submillimeter frequencies. The black trace is the sequence of 288 MHz bandwidth chirped pulses, which are used to excite molecular transitions, 25 ns in duration, followed by a period where the second AWG channel (blue trace) is used as the local oscillator to detect the FID signals. Because the two AWG channels step by the same amount from segment to segment, all molecular transitions are detected in the same narrow (in this case, 288 MHz) spectral bandwidth.

### 3. Results and discussion

The result of a single acquisition cycle of this experiment, acquired in  $58 \mu\text{s}$ , is shown in Figs. 3 and 4, compared to a simulated spectrum at 300 K generated from the JPL spectral catalog [22]. The signal-to-noise ratio of the strongest transition in this spectrum is approximately 120:1. At a pressure of 40 mTorr, collisional self-broadening dominates the free induction decay rate, which has a time constant of approximately 100 ns. The  $T_2$  time of methanol in this frequency range in the low-pressure limit (i.e., due only to Doppler broadening) is approximately 500 ns. In addition to the line broadening induced by the high pressure, the linewidths in CP-mmW spectroscopy exceed those of absorption spectroscopy by a factor of 3 for reasons that are described in detail elsewhere [16]. As in past implementations of chirped-pulse millimeter-wave spectroscopy, time-domain signal averaging can be performed

to enhance the sensitivity. This instrument was found to have good phase stability, demonstrated by preservation of the signal intensity when co-adding 1000 FID traces.

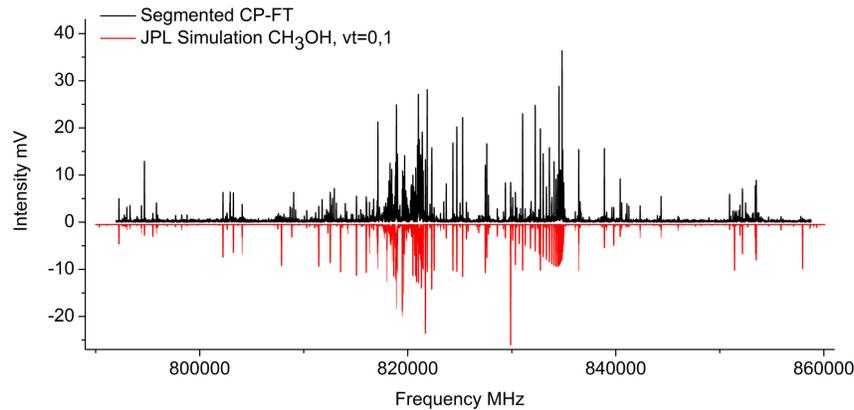


Fig. 3. Single acquisition cycle (58  $\mu$ s data collection) of methanol (black) with 67 GHz bandwidth, compared to a simulation at 300 K generated using the JPL spectral catalog [22] (red).

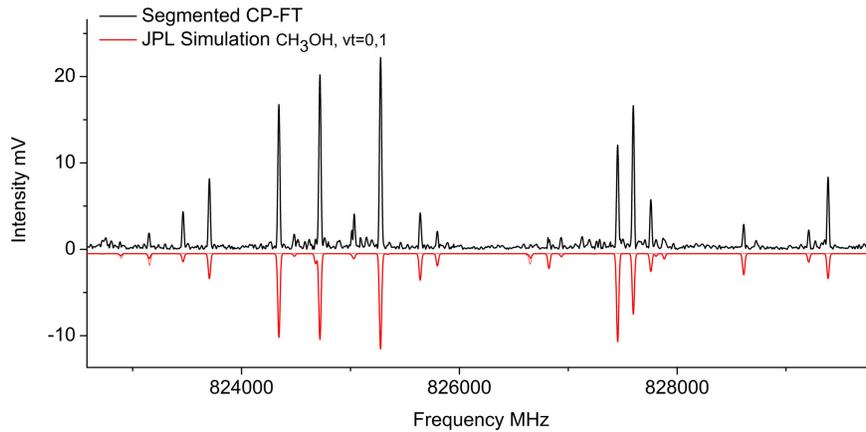


Fig. 4. Expanded view of the 67 GHz 58  $\mu$  sec single shot segmented CP-FT spectrum of methanol (black) compared to the JPL simulation.

Submillimeter spectroscopy with the segmented CP-FT technique has some significant advantages when compared to the previously described single LO approach. When dividing a spectrum into  $N$  segments by this method, a single spectral acquisition cycle takes a factor of  $N$  longer than when the entire spectral bandwidth is addressed by a single chirp. Segmented CP-FT spectroscopy, however, takes advantage of the fact that the AMC power is far below that required to saturate molecular transitions of most molecules in this frequency range given the limitation on the duration of the excitation pulse set by the  $T_2$  dephasing time. In the weak pulse limit, the signal strength scales with the inverse of the square-root of the sweep rate,  $(dv/dt)^{-1/2}$  [12,23]. Therefore, because the bandwidth of the excitation pulse is reduced by  $N$ , the absolute signal level in each segment is  $\sqrt{N}$  higher than when the entire spectral bandwidth is addressed by a single chirp. In order for the unsegmented measurement to reach the same sensitivity as the segmented one,  $N$  signal averages must be performed in order to recover this factor of  $\sqrt{N}$ . Therefore, in the weak pulse limit, the data acquisition time

required to reach a given sensitivity level across a given spectral bandwidth is independent of the number of segments into which the spectrum is divided.

The full-band CP-FT, single oscillator approach signal averages 2 microsecond acquisitions at a rate of 400 Hz [16]. The rate is limited by data transfer of each acquisition to stored memory. A real-time rate with no overhead time between 2 microsecond acquisitions would be 500 kHz. There is room for a 1,000 fold improvement in duty cycle that can be addressed by segmenting the acquisition. The oscilloscope sampling requirement is much lower when segmenting due to the low detection bandwidth. As result, technology that is more practical in terms of form factor, cost, and data processing rate can be utilized for broadband spectrum analysis. PCIe digitizer cards with sample rates up to 4GS/s are available with field programmable gate array (FPGA) accumulators. This pairing of technology promises practically real-time signal averaging by accumulating successive acquisitions into the memory buffer before transfer. There is also a reduction in computing overhead that results in the Fourier transformation stage by segmenting and parallelizing the computation, as the number of computations in the fast Fourier transform algorithm scales as  $O(n \log n)$ . The 790 – 860 GHz spectrum differs in experiment time (250 nanosecond FID collection) compared to the full-band CP-FT (260-290 GHz) presented previously in the literature (2 microsecond FID collection). However, the same principles apply. The band can be addressed using one 250 nanosecond full-band chirped pulse acquisition, or many segmented 250 nanosecond acquisitions. The experiment presented here used an IF frequency range of 4032-4320 MHz and a 40 GS/s oscilloscope. This IF frequency range was chosen to minimize the spurious output of the SHM. However, in this proof-of-principle measurement, the 67 GHz of spectral bandwidth was still acquired with 232 segments having a detection bandwidth of only 288 MHz. A second mixing stage (double conversion superheterodyne) can be employed to bring this frequency range closer to DC so that a lower sampling rate oscilloscope can be used to fully realize these speed and cost advantages.

The current limitation of the segmented CP-FT approach as compared to the single full-band sweep is the spurious signal content in the AWG LO channel. In Figs. 3 and 4, the simulated spectrum in red incorporates transitions from CH<sub>3</sub>OH in its ground vibrational state as well as its first torsionally excited state. There are a number of weak lines that are not found in the simulation. Some of these lines are likely due to transitions in higher-energy vibrational levels that are not yet included in the spectral database; it has been estimated that the strongest unassigned transitions of methanol are a factor of 37 weaker than the strongest overall transitions [24], which would make them visible in a single acquisition. The technique is very sensitive to the spurious content of the LO signal in the heterodyne sub harmonic mixer. Strong molecular signals can mix with spurious signals to create image lines that fall within the detection bandwidth; we are particularly sensitive to very low-frequency spurs (less than the segment bandwidth), as these image lines will fall near the molecular signal. In Fig. 4, the weak spurs (which appear almost as an artificial noise floor) seem to be concentrated near the strong molecular lines. Spurs that carry through the mixer also appear in the spectrum if they fall within the IF bandwidth of a segment. The effect of spur carriers is compounded by the fact that, depending on the cause of the spurs, they reappear in each new segment until they “walk” out of the 288 MHz IF band. For conventional CP-FT, the LO remains at a constant frequency, so a very tight band pass filter can be used to screen out the spurious content of the AWG generated LO [16]. For segmented CP-FT, because the LO frequency is changing rapidly with time, we cannot impose a narrow bandpass filter around each segment; instead, a single filter that has as its band pass the entire spectral region covered in the experiment must be used. High spectral purity in the AWG, critical for segmented CP-FT, continues to be the focus for significant performance improvement with each new generation of AWGs.

#### **4. Conclusion**

Segmented CP-FT spectroscopy is an effective way to implement chirped pulse Fourier transform methods at millimeter/submillimeter wavelengths. By reducing the data throughput, without sacrificing the amount of time required to reach a given sensitivity across a broad bandwidth, this technique reduces the processing time currently inherent to CP-FT spectroscopy [16]. This technique is particularly powerful for static gas samples where 100% duty cycles can be employed. The reduction in cost associated with a lower-bandwidth digitizer is also significant and may enhance the general applicability of the chirped pulse spectroscopic technique.

#### **Acknowledgment**

This work was supported by the NSF Centers for Chemical Innovation program through CHE-0847919 and by the National Science Foundation Graduate Research Fellowship under grant No. DGE-0809128. Additional support was provided by the University of Virginia.