Fourier Transform Spectrometry with a Near-Infrared Supercontinuum Source

CHRIS A. MICHAELS,* TONY MASIELLO,† and PAMELA M. CHU

Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Optical fiber based supercontinuum light sources combine the brightness of lasers with the broad bandwidth of incandescent lamps and thus are promising candidates for sources in spectroscopic applications requiring high brightness and broad bandwidth. Herein, near-infrared (IR) Fourier transform (FT) spectrometry with a supercontinuum (SC) light source is investigated. The efficient, collimated propagation of broad bandwidth SC light through an 18 m path length multipass cell is demonstrated. A normalized spectral difference is calculated for the SC spectrum on consecutive FT mirror scans and is found to vary by less than 0.5%, indicating excellent spectral stability. The rms noise on zero absorbance lines is obtained as a function of the number of mirror scans at 0.125, 2, and 16 cm^{-1} resolution for both the SC and conventional tungsten lamp source. The SC source has approximately a factor of ten times more noise than the lamp under comparable conditions for each resolution and data acquisition time. This clearly indicates that spectral acquisition with the SC source is not detector noise limited. NIR-FT spectra of methane and methyl salicylate, acquired with both the SC and lamp source, are reported. These spectra illustrate the advantage the SC source has over the incandescent source in that it can efficiently traverse long path lengths, thus providing a sensitivity advantage. The spectra also demonstrate the disadvantage of the SC source with respect to the lamp in the increased level of amplitude noise. Prospects for the future use of SC sources in absorption spectroscopy, including possible noise mitigation strategies, are briefly discussed.

Index Headings: **Near-infrared spectroscopy; NIR spectroscopy; Supercontinuum radiation; Fourier transform infrared spectroscopy; FT-IR spectroscopy.**

INTRODUCTION

Incandescent light sources have long been utilized in infrared (IR) spectroscopy, both in the mid-infrared (MIR), where references to the ubiquitous globar date to at least 1929,[1] and in the near-infrared (NIR), where a quartz tungsten halogen lamp has long been the standard choice. These sources are cheap, compact, and powerful; they are and will continue to be the workhorses of IR spectroscopy. However, there are some applications for which thermal sources are poorly suited. High resolution spectroscopy of gases is an application in which the narrow bandwidth of certain types of IR lasers (e.g., lead salt[2] and quantum cascade[3] lasers) has been exploited. Another class of applications requires higher brightness levels than can be provided by an incandescent source that, while radiating high power levels, does so into all directions (4π steradians), as opposed to the collimated output of a laser. Examples of these applications include long path length absorption spectroscopy that requires collimated long distance propagation[4] or microscopy in the near-field[5] or even at diffraction limited spot sizes.[6] Typically lasers are chosen for these applications, effectively addressing the brightness deficiency while reducing the bandwidth of the source. This is not a trivial trade-off as the power of IR spectroscopy as an analytical tool is often dependent on measuring the sample response across a broad spectral range. The ideal source for these applications would have laser brightness coupled with the bandwidth of a thermal source. In fact, synchrotron radiation does possess this combination of qualities to some degree and has been exploited for diffraction-limited IR microscopy.[7] Naturally, a comparable, portable light source would be highly desirable.

In 2000, the efficient generation of so-called visible supercontinuum (SC) radiation by pumping photonic crystal fibers (PCF) with ultrafast, nanojoule laser pulses was reported.[8,9] A report of SC generation in mechanically tapered fibers followed shortly thereafter.[10] These light sources have octave spanning bandwidth emitting from the near diffraction limited core of the optical fiber, thus effectively mimicking a near point source. Consequently, these sources possess very high brightness, enabling efficient collimation for long distance propagation and diffraction-limited focusing. Subsequent work has broadened the types of pump sources and fibers used and has expanded the spectral ranges over which these devices function.[11] These spectral ranges include the NIR, for which commercial products are now available, and to a limited extent the MIR, wherein the absorption losses in silica-based fibers dictate recourse to less conventional fiber materials, including chalcogenides,[12] fluorides,[13–15] and tellurite PCFs.[16] Picqué and co-workers have recently reported on the use of a laboratory-constructed NIR supercontinuum source for high resolution Fourier transform infrared (FT-IR) spectroscopy of gases.[17] Given the increasing availability of commercial SC light sources it is timely to investigate further the question of whether they are suitable for FT-IR spectroscopy in applications that require high brightness and to compare their performance against standard incandescent sources.

It is instructive to briefly consider the physical processes that give rise to supercontinuum generation in optical fibers. In general, a combination of phenomena including stimulated Raman scattering, soliton fission, self-phase modulation, modulation instability, and dispersive wave generation lead to SC generation. The relative importance of each process is dependent on the pump wavelength and pulse width along with the dispersion properties of the fiber.[11] It is reasonable to presume that the nonlinear nature of the SC generation process might lead to significant amplitude variation in the output, particularly given that the pulsed pump sources also typically have non-trivial amplitude fluctuations. This has potentially significant consequences for FT spectrometry if the noise spectrum of the source has significant amplitude at the frequencies relevant to the interferogram. This type of noise (fluctuation noise) is multiplicative in Fourier spectroscopy,[18] likely compromising the ultimately attainable signal-to-noise

Received 23 September 2008; accepted 18 February 2009.
* Author to whom correspondence should be sent. E-mail: chris.Michaels@nist.gov.
† Present address: Department of Chemistry and Biochemistry, California State University, East Bay, Hayward, CA 94542.

0003-7028/09/6305-0538$2.00/0

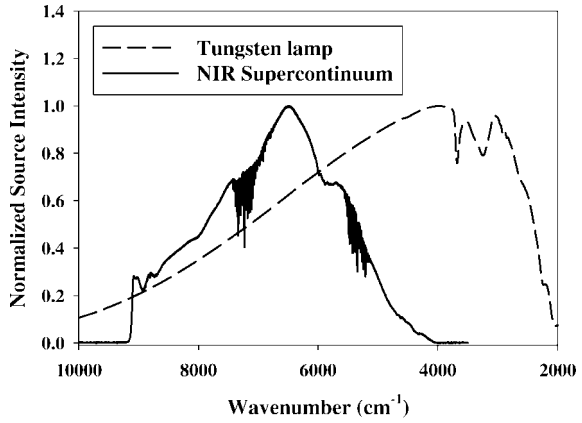

FIG. 1. FT-IR spectra of NIR supercontinuum source (solid line) and tungsten lamp (dashed line) with peak amplitude normalized to one.

(S/N) ratio. Notably, there are cancellation strategies for this type of noise but they are not straightforward to implement using the interferometer designs that currently dominate the commercial FT-IR market.[19] The noise issue is potentially a major hurdle for implementation of these sources and thus a quantitative understanding of their noise characteristics is critical to evaluating their potential utility.

This paper describes an evaluation of the performance of a commercial SC source in NIR-FT spectrometry in an application that requires high brightness. The noise on so-called zero absorbance lines recorded with an SC source is compared to those recorded with a conventional lamp source at various resolutions as a function of the number of mirror scans. The spectra of several gases are recorded using a 18 m multipass cell with the SC source. These spectra are benchmarked against spectra measured with a tungsten lamp source in a 2 m cell with similar analyte concentrations. These data allow an assessment of the practical utility of current generation NIR SC sources in FT spectrometry. Experimental conditions in which these sources show some advantage over the conventional sources will be discussed along with some possible directions for further development.

EXPERIMENTAL

The NIR SC source generates up to 6 W of light spanning wavelengths from 450 nm to 2500 nm at a repetition rate of 80 MHz. The light is coupled into a transport fiber inside the laser housing and exits the fiber into a collimating lens. The light is then steered into a multipass absorption gas cell, based on an astigmatic variant of the off-axis Herriot configuration,[20] aligned in the 90 pass configuration, yielding a path length of 18 m. The input aperture radius of this cell is 0.44 cm. The light exiting the cell is attenuated with broadband neutral density filters to avoid detector saturation and spectrally filtered to remove residual light at the pump wavelength (1064 nm) and shorter wavelengths. This is done to preserve the dynamic range of the detector by eliminating any response due to spectral intensity outside the range of interest. The SC light is inserted into the beam path of an FT-IR (Bruker IFS 66V)[‡] following the last curved mirror, ensuring collimated propagation through the Michelson interferometer. A silicon coated, CaF_2 beam splitter is used along with an Indium Antimonide detector. In general, the attenuation was varied to allow full use of the A/D converters of the detection circuit with the lowest gain. Notably, even after 18 m propagation there was ample overhead from the 6 W source such that significant attenuation was required. The lamp spectra were recorded using a 2 m path length cell inserted into the sample compartment of the FT-IR spectrometer. The same detector was utilized and the amplifier gain settings were matched to those used in the SC measurements to the extent possible. The spectra and zero absorbance lines were recorded in rapid scan with resolutions of 0.125, 2, and 16 cm^{-1}, using a helium-neon laser modulation frequency of 40 kHz with signal averaging over the number of mirror scans noted in the text. A Jacquinot stop was not used for the measurements taken with the SC source, while a 0.5 mm stop was used for acquisition of spectra with the lamp source at 0.125 cm^{-1} resolution. Note that the 80 MHz pulse frequency of the laser source is essentially continuous wave (cw) with respect to the Fourier modulation frequencies. A three-term Blackman–Harris apodization function was utilized.

The noise impacting measurements made with the two sources was evaluated by analysis of so-called zero absorbance lines,

$$A_0^x = -\log\left(\frac{I_x}{I_y}\right) \quad (1)$$

where x represents the number of mirror scans and y is the number of scans utilized for the background. The value of y was chosen to minimize noise due to the background. In the case of the 2 and 16 cm^{-1} resolution series, x ranged from 2 through 512 with a y value of 1024, wherein the case of the 0.125 cm^{-1} resolution series x ranged from 2 through 128 with a y value of 256. The rms noise level was quantified by calculating the standard deviation in A_0^x over the spectral range from 6000 to 6800 cm^{-1}, near the peak of the SC source spectrum.

Spectra were obtained for gas samples from several sources including a gas cylinder mixture of 0.19% CH_4 in N_2,[§] and methyl salicylate (MES) in nitrogen. The MES vapor stream was prepared by flowing nitrogen at 0.2 L min^{-1} through a saturation cell containing liquid MES. The saturation cell was maintained at 20 °C by a temperature-controlled bath. The mole fraction of MES in the vapor stream was approximately 100 μmol mol^{-1}.

RESULTS AND DISCUSSION

Figure 1 is a plot of the SC source spectrum compared to that of the traditional tungsten lamp source spectrum as measured in the FT-IR where the respective peak intensities have been set equal to 1 to facilitate comparison. The apparent short wavelength cut-off in the SC source spectrum is due to the long-pass filter used to exclude SC pump laser radiation (1064 nm) while the long wavelength edge is a measure (modified by the instrument response function of the FT-IR) of the declining efficiency of the SC generation process at long wavelengths. This decline is presumably largely due to material absorption in

[‡] Certain commercial products or equipment are identified so as to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply that it is necessarily the best available for the purpose.

[§] The 0.19% CH_4 in N_2 gas cylinder mixture was prepared at NIST in conjunction with the gas standards reference materials program (2008).

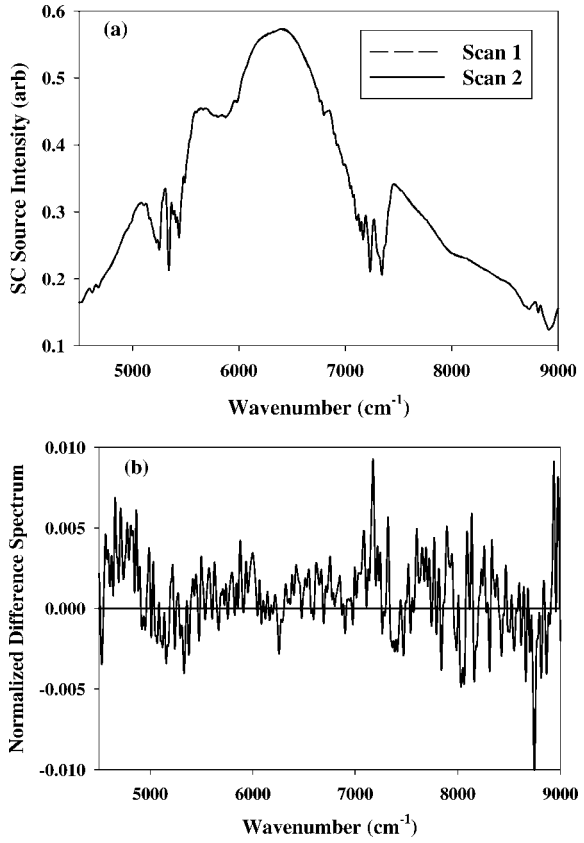

FIG. 2. (**a**) Two indistinguishable FT-IR spectra of supercontinuum source (solid and dashed) acquired in consecutive single mirror scans at 2 cm^{-1} resolution. (**b**) Normalized spectral difference (see definition in Eq. 2) between scan 1 and 2 spectra shown in (a).

the nonlinear fiber. The water overtone bands, centered around 7200 and 5300 cm^{-1}, respectively, are present in the SC spectrum as it was not possible to purge the spectrometer in the configuration employed to allow insertion of the SC beam at the appropriate point in the interferometer. This issue could be resolved if required; however, the gas species measured for this work have bands lacking significant overlap with the water overtones.

Clearly the SC source has comparable bandwidth in the NIR region to the tungsten lamp, sufficient to measure a wide variety of species with significant absorption features in this region. The other important feature of the spectra lies in the path length traversed for each source. The SC source light propagated through a multipass cell of 18 m path length with enough efficiency that significant attenuation was still required to avoid detector saturation. It is instructive to consider the relative spectral intensities measured for the SC source and the tungsten lamp. Neutral density of 2 (attenuation of 100×) was required to yield comparable signals at the detector after the SC source propagated through the 18 m multipass cell (90 reflections) and light from the tungsten source propagated through the 2 m cell (19 reflections). This is a realization of one of the postulated benefits of utilizing a supercontinuum as a spectroscopic source; collimated propagation akin to that of a laser, with the bandwidth of an incandescent source. No measurements have yet been undertaken to assess the limits on what path lengths might be accessible with this source, but certainly another order of magnitude greater than that demonstrated here (>100 m) seems quite plausible. Indeed, a recent report demonstrates the use of a NIR SC for open path monitoring using dispersive detection over a 300 m path length.[21] This strongly suggests that supercontinuum sources have the potential to greatly impact the utility of NIR FT spectroscopy in open path monitoring and stand-off detection applications. However, a quantitative understanding of source noise is clearly required for a full assessment of the potential of SC sources in this type of application.

An immediate question raised by Fig. 1 is how stable the SC spectrum is from mirror scan to mirror scan. That is, is the overall spectral shape changing significantly on the time scale of the mirror scan? A series of single scan spectra were recorded at resolutions of 0.125, 2, and 16 cm^{-1}. In general, the reproducibility of the spectral shape from scan to scan was excellent at each resolution and overlain spectra were difficult to differentiate. This is illustrated in Fig. 2a, in which two consecutively recorded single mirror scan spectra at 2 cm^{-1} resolution are plotted over the spectral range of 4500 to 9000 cm^{-1} (the spectral region for which there is significant source intensity). The time gap between the measurements was on the order of 30 s. The differences are generally smaller than the line thickness in the plot, making visual distinction of the two spectra essentially impossible. To evaluate the variation quantitatively, a normalized spectral difference, $D(\nu)$, was calculated at each frequency,

$$D(\nu) = \frac{I_1(\nu) - I_2(\nu)}{I_1(\nu)} \tag{2}$$

where $I_n(\nu)$ is the intensity recorded in scan n at the wavenumber ν. Note that this quantity is just $[1 - T(\nu)]$ where T is the transmittance. This quantity is plotted in Fig. 2b for the scans shown in Fig. 2a. (Note that there is some unknown type of low frequency modulation in the data that makes the spectra appear smoothed beyond what would be expected at 2 cm^{-1} resolution). The source of this modulation is unknown. Aside from a few outlying points, the differences stayed within plus or minus a half percent and there is no systematic variation with frequency as one would expect for significant shifts in spectral shape. These observations apply equally well to the data taken at 0.125 and 16 cm^{-1} resolution, indicating that the spectral character of the SC source output is temporally stable, at least for the time scales relevant to the FT mirror scans.

To further the exploration of noise in the SC source in comparison to that in the tungsten lamp, the series of zero absorbance lines described earlier was analyzed. Figure 3 shows the relationship between the rms noise and number of scans over a series of zero absorbance line acquisitions for both the SC source and the tungsten lamp taken at 0.125 cm^{-1} resolution. Note that these measurements reflect transmission through the 18 m path cell in the case of the SC and the 2 m path cell in the case of the tungsten lamp. The values are plotted on a log–log scale to allow for easy comparison of the two sources. The solid line indicates the relationship expected in the detector noise limited regime wherein, assuming constant signal levels, the zero absorbance line rms noise drops proportionally to the square root of the measurement time or, in this case, the number of mirror scans.[18] Note that deviation from this line indicates the presence of noise sources other than the detector. The SC source is roughly an order of magnitude noisier than the tungsten lamp source across the entire range of mirror scans indicating that source, or fluctuation noise, is an

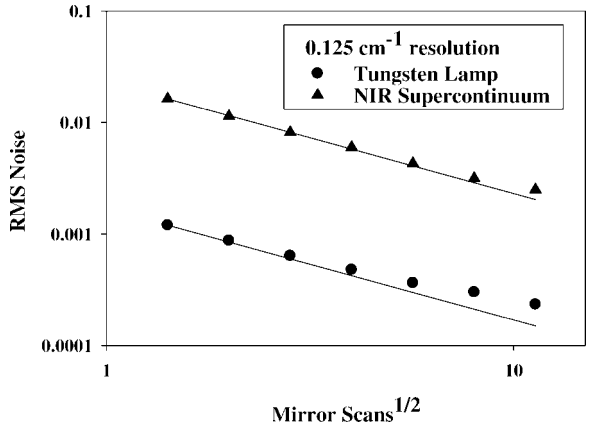

FIG. 3. Log–log plot of rms noise on a series of zero absorbance lines recorded at 0.125 cm^{-1} resolution plotted against the square root of the number of mirror scans for the tungsten lamp source (triangles) and the supercontinuum source (circles). Solid line indicates expected scaling in detector noise limited regime.

important component of the overall noise in the SC case. This is a clear indication that detector noise is not the limiting source of noise in the SC case and thus this is not an optimal source for FT-IR spectrometry from the perspective of noise reduction. This observation also applies to similar data series recorded at resolutions of 2 cm^{-1} and 16 cm^{-1}. This finding has significant ramifications for the use of these sources in FT-NIR spectroscopy as ultimately the greater noise floor for the SC source will limit the sensitivity attainable with this source.

Two significant findings regarding the characteristics of a commercial NIR SC laser utilized as a source for FT spectroscopy have been described thus far. First, the SC source can propagate in a collimated manner over long distances (>>18 m), distance regimes that are challenging with incandescent sources.[22] Note that the measured divergence angle for the SC source is nominally 0.5°.[23] This opens up new possibilities in open path monitoring and stand-off detection or the prospect of enhanced sensitivity in trace gas detection in multi-pass configurations. However, this advantage is mitigated to some extent by the presence of source noise that increases the noise floor about a factor of ten over that of a conventional source. This suggests that the SC might be the best source in cases where the path length advantage is exploited to an extent sufficient to outweigh the source noise disadvantage, or when long distance propagation is a necessity and an incandescent source is unable to deliver sufficient photon flux to the detector. However, in applications involving typical laboratory-scale short path lengths, the SC source is clearly at a disadvantage due to the source noise (not to mention cost). As a means of further illustrating the tradeoffs between path length and noise, the spectra of several gases were recorded with the conventional tungsten lamp source and the SC and compared.

Near-infrared spectra of methane (0.2% in N_2) were recorded at 0.125 and 2 cm^{-1} resolution in order to illustrate the performance of the SC source in applications relevant to trace, small gas molecule monitoring. The total pressure in the multipass cells was 100 torr for the 0.125 cm^{-1} resolution data where the data is averaged over 256 mirror scans. These spectra are shown in Fig. 4a wherein the top spectra is that recorded with the lamp source (2 m path) while the bottom spectra is that recorded with the SC source (18 m path). Note

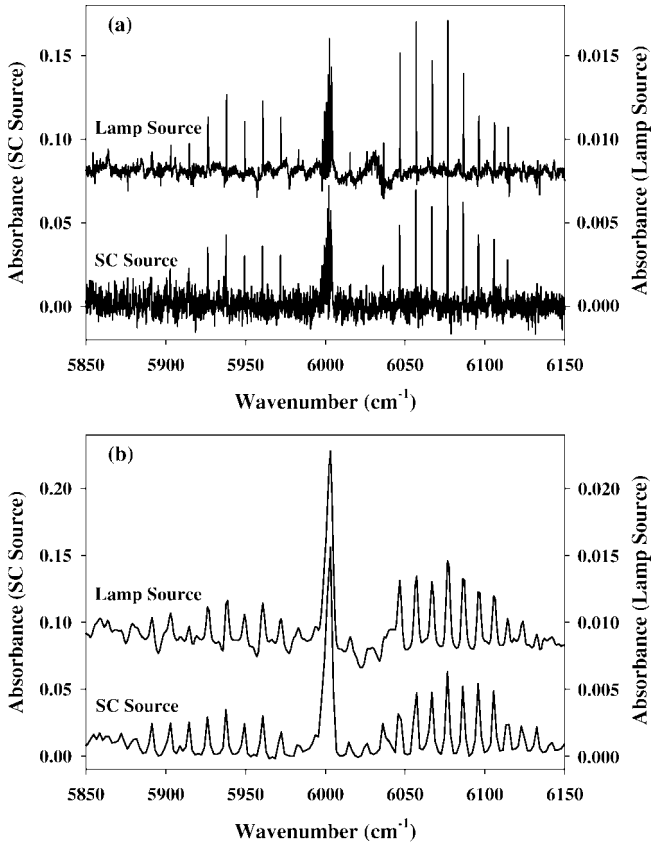

FIG. 4. (**a**) FT-IR spectra of $2\nu_3$ overtone band of methane acquired at 0.125 cm^{-1} resolution with the tungsten lamp source (upper spectrum, right *y*-axis scale) and with the supercontinuum source (lower spectrum, left *y*-axis scale). The total pressure was nominally 100 Torr of 0.2% methane in N_2 in a multipass cell of path length 2 m (tungsten lamp) or 18 m (supercontinuum). (**b**) FT-IR spectra of $2\nu_3$ overtone band of methane acquired at 2.0 cm^{-1} resolution with the tungsten lamp source (upper spectrum, right *y*-axis scale) and with the supercontinuum source (lower spectrum, left *y*-axis scale). The total pressure was nominally 760 torr of 0.2% methane in N_2 in a multipass cell of path length 2 m (tungsten lamp) or 18 m (supercontinuum).

that the absorbance values for the lamp source are described by the right *y*-axis tick labels, a factor of ten lower than those of the SC source shown on the left *y*-axis tick labels. Additionally the lamp source spectrum is offset vertically to facilitate visual comparison. The absorbance values reflect the longer path length for the SC measurement as they appear to be slightly less than a factor of ten greater than those of the lamp spectrum, in reasonable agreement with the 9:1 path length ratio between the two cells. These spectra encompass the P, Q, and R branches of the 1.66 μm $2\nu_3$ overtone band of methane.[24] The data shown in Fig. 3, coupled with the path length difference in the two cells, suggest that the S/N ratios in these spectra should be approximately the same, as the noise floor is nominally a factor of ten higher in the SC case, roughly canceling the increased signal level due to the longer path length. The S/N in the SC methane spectra is somewhat worse than the lamp spectra, although the expectations for similar S/N are based only on approximate considerations. The character of the noise is different in the two spectra, with the lamp spectra showing a relatively low frequency ripple (likely due to an etalon originating from the cell) along with a high frequency component similar to that dominating the SC spectrum. These spectra nicely capture the strengths and weaknesses of the SC

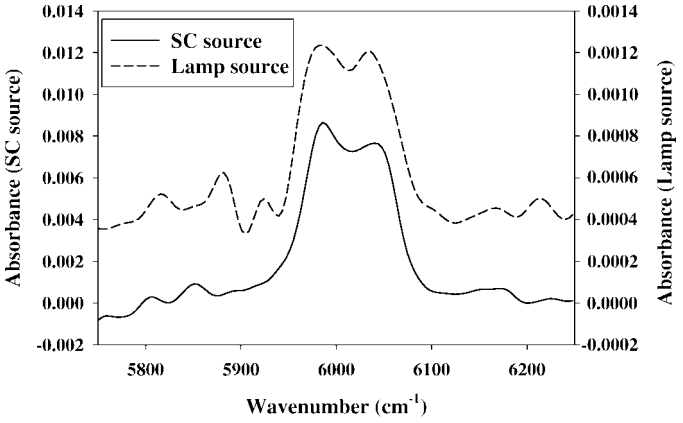

FIG. 5. FT-IR spectra of a methyl salicylate overtone band acquired at 16.0 cm^{-1} resolution with the tungsten lamp source (upper spectrum, dashed line, right *y*-axis scale) through a 2 m path length and with the supercontinuum source (lower spectrum, solid line, left *y*-axis scale) through an 18 m path length.

source compared to the lamp. The SC source is impacted by a higher noise level yet it can be effectively deployed over much longer path lengths, which can compensate for the noise disadvantage.

Figure 4b shows comparable spectra of the $2\nu_3$ overtone band region of methane taken at 2 cm^{-1} resolution over 1024 mirror scans for which the total pressure in the multipass cells was nominally 760 torr. As in Fig. 3a the lamp source spectrum (top) is described by the *y*-axis labels on the right while the SC source spectrum (bottom) is described by those on the left. Note that there again appears to be some secondary spectral structure in the lamp spectrum that is, in this case, demonstrably absent from the SC spectrum. Nevertheless, the spectra are generally quite comparable.

Figure 5 shows the near-infrared overtone spectrum of MES acquired at 16 cm^{-1} resolution. This analyte was chosen to evaluate the utility of this source in detection of larger volatile organic molecules, for which low spectral resolution is adequate. As in Fig. 4 the lamp source spectrum (top) is described by the *y*-axis labels on the right while the SC source spectrum (bottom) is described by those on the left. As in the previous spectra, the absorbance magnitudes differ by roughly the amount expected on the basis of the path length differences. The spectra are generally comparable, suggesting that the SC source might prove valuable in applications involving low resolution detection of large molecules in open-path standoff detection applications.

An interesting side-note to these spectra is that the visible portion of the SC radiation apparently photolyzed the MES in the multipass cell. When the filter used to block the light to the high energy side of the pump wavelength (1064 nm down through the visible) was placed after the multipass cell, the MES signal disappeared. Placing the filter prior to the multipass cell resulted in the reappearance of the signal from the MES flowing through the cell. The overall intensity of the source is quite high (6 W) and a significant fraction of that power is distributed over the visible spectrum. Little intensity is emitted at wavelengths less than 450 nm; absorption losses in the fiber are likely to be significant in this region. This observation might prove relevant to other analytes and also points to possible concerns for applications where eye-safe deployment is an issue. Nevertheless, proper spectral filtering can mitigate this issue.

An outstanding question is what size reduction in SC source noise is possible with improvements in design. In the best case, the SC noise level might be reduced to that of the shot noise on the pump laser and the spontaneous Raman scattering in the fiber amplified by the operative nonlinear processes giving rise to SC generation.[25] To what extent currently available sources approach this limit is not clear, particularly given the variety of processes involved in SC generation. It may be the case that these fundamental noise sources will ultimately limit the utility of SC in FT detection schemes. However, a number of mitigation strategies are possible. In particular, some strategy for real-time noise cancellation, either using matched detectors or a dual beam interferometer,[19] should yield some improvement. Alternatives to FT detection could also prove to be useful platforms for exploring source noise mitigation strategies. Advances in IR detector materials have enabled recent advances in dispersive detection techniques using a diffraction grating and planar array detector.[26] Additionally, the use of long fibers of known dispersion coupled with high speed detection electronics to detect the spectrum of light transmitted through the fiber in the time domain has also recently been reported.[27] Clearly further work is required to assess the viability of these strategies for noise reduction with an SC source.

Given the novelty of this source technology, it is reasonable to expect the design improvements in the SC itself might also yield lower levels of source noise. However, even if fundamental limitations on the source noise limit the ultimate performance of SC sources in conventional FT spectrometry, strategies to compensate for this noise exist. Another potential advance may be found in the development of MIR SC sources, which would allow spectrometry with fundamental vibrational bands. Of course, this would yield large increases in sensitivity and greater chemical specificity. Accordingly, the development of sources in this spectral region is being pursued by a number of groups.[12–16] It seems clear that, at least in applications that demand SC brightness, this new source technology has great potential.

ACKNOWLEDGMENTS

The authors would like to thank Steve Brown for making the SC source available for these measurements. Additionally, the authors would like to thank the NIST Gas Metrology Group for the CH_4 in N_2 cylinder sample and the U.S. Department of Homeland Security Science and Technology Directorate for partial support of this work.

1. E. K. Plyler, Phys. Rev. **33,** 48 (1929).
2. E. T. Sevy, C. A. Michaels, H. C. Tapalian, and G. W. Flynn, J. Chem. Phys. **112,** 5844 (2000).
3. K. Namjou, S. Cai, E. A. Whittaker, J. Faist, C. Gmachl, F. Capasso, D. L. Sivco, and A. Y. Cho, Opt. Lett. **23,** 219 (1998).
4. H. I. Schiff, G. I. Mackay, and J. Bechara, in *Air Monitoring by Spectroscopic Techniques*, M. W. Sigrist, Ed. (John Wiley and Sons, New York, 1994), Chap. 5.
5. C. A. Michaels, X. H. Gu, D. B. Chase, and S. J. Stranick, Appl. Spectrosc. **58,** 257 (2004).
6. C. A. Michaels, Appl. Phys. Lett. **90,** 121131 (2007).
7. N. Jamin, P. Dumas, J. Moncuit, W. H. Fridman, J. L. Teillaud, G. L. Carr, and G. P. Williams, PNAS **95,** 4837 (1998).
8. J. K. Ranka, R. S. Windeler, and A. J. Stentz, Opt. Lett. **25,** 25 (2000).
9. W. J. Wadsworth, J. C. Knight, A. Ortigosa-Blanch, J. Arriaga, E. Silvestre, and P. S. J. Russell, Electron. Lett. **36,** 53 (2000).
10. T. A. Birks, W. J. Wadsworth, and P. S. Russell, Opt. Lett. **25,** 1415 (2000).

11. J. M. Dudley, G. Genty, and S. Coen, Rev. Mod. Phys. **78,** 1135 (2006).
12. J. S. Sanghera, I. D. Aggarwal, L. B. Shaw, C. M. Florea, P. Pureza, V. Q. Nguyen, F. Kung, and I. D. Aggarwal, J. Optoelectron. Adv. Mat. **8,** 2148 (2006).
13. C. Xia, M. Kumar, M. Y. Cheng, R. S. Hegde, M. N. Islam, A. Galvanauskas, H. G. Winful, F. L. Terry, M. J. Freeman, M. Poulain, and G. Maze, Opt. Exp. **15,** 865 (2007).
14. C. A. Xia, M. Kumar, O. R. Kulkarni, M. N. Islam, F. L. Terry, and M. J. Freeman, Opt. Lett. **31,** 2553 (2006).
15. C. L. Hagen, J. W. Walewski, and S. T. Sanders, IEEE Photon. Tech. Lett. **18,** 91 (2006).
16. P. Domachuk, N. A. Wolchover, M. Cronin-Golomb, A. Wang, A. K. George, C. M. B. Cordeiro, J. C. Knight, and F. G. Omenetto, Opt. Exp. **16,** 7161 (2008).
17. J. Mandon, E. Sorokin, I. T. Sorokina, G. Guelachvili, and N. Picque, Opt. Lett. **33,** 285 (2008).
18. P. R. Griffiths and J. A. de Haseth, *Fourier Transfrom Infrared Spectroscopy* (Wiley Interscience, New York, 2007), 2nd ed.
19. W. J. Burroughs and J. Chamberlain, Infrared Phys. **11,** 1 (1971).
20. J. B. Mcmanus, P. L. Kebabian, and W. S. Zahniser, Appl. Opt. **34,** 3336 (1995).
21. D. M. Brown, K. B. Shi, Z. W. Liu, and C. R. Philbrick, Opt. Exp. **16,** 8457 (2008).
22. S. N. Mikhailenko, V. G. Tyuterev, V. I. Starikov, K. K. Albert, B. P. Winnewisser, M. Winnewisser, G. Mellau, C. Camy-Peyret, R. Lanquetin, J. M. Flaud, and J. W. Brault, J. Mol. Spectrosc. **213,** 91 (2002).
23. S. W. Brown, Personal Communication (2008).
24. G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945), p. 306.
25. K. L. Corwin, N. R. Newbury, J. M. Dudley, S. Coen, S. A. Diddams, K. Weber, and R. S. Windeler, Phys. Rev. Lett. **90,** 113904 (2003).
26. I. Pelletier, C. Pellerin, D. B. Chase, and J. F. Rabolt, Appl. Spectrosc. **59,** 156 (2005).
27. J. Hult, R. S. Watt, and C. F. Kaminski, Opt. Exp. **15,** 11385 (2007).