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Octave-spanning mid-infrared pulses by plasma generation in air pumped with an Yb:KGW source

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Abstract

Femtosecond mid-infrared (IR) supercontinuum generation in gas media provides a broadband source suited for time-domain spectroscopies and microscopies. This technology has largely utilized <100 fs Ti:sapphire pump lasers. In this Letter, we describe the first plasma generation mid-IR source based on a 1030 nm, 171 fs Yb:KGW laser system; when its first three harmonics are focused in air, a conical mode supercontinuum is generated that spans <1000 to 2700 cm^{-1} with a 190 pJ pulse energy and 0.5% RMS stability.

Source development has driven the evolution of ultrafast infrared (IR) spectroscopies and microscopies capable of probing molecular structure on the timescales of its fastest motions with spatial resolution [1-7]. The most developed ultrafast mid-IR sources rely on optical parametric amplification (OPA) and difference frequency generation (DFG) to convert the near-IR output of a femtosecond amplifier. The typical bandwidth of the OPA + DFG approach is $\nu = 100 - 600 \text{ cm}^{-1}$. As time-domain techniques are suited for broad spectral sources, there is an increasing need for continua spanning the mid-IR ($\nu 100 - 4000 \text{ cm}^{-1}$). Plasma-based sources are developing as an alternative to OPA + DFG that compromises conversion efficiency for bandwidth. In the plasma-based approach, ultrabroad pulses are generated in a single step by cascaded four-wave mixing processes in low-dispersion, high-damage threshold gas media [8]. Cook and Hochstrasser first observed terahertz emission by focusing the first and second harmonic of a 65 fs, amplified Ti:sapphire (Ti:S) laser in air [9]. In 2007, Fuji and Suzuki extended this work to the mid-IR region [10]. A selection of relevant advances in this broadband IR continuum generation technology are summarized in Table 1, including the use of different gas phase media and multiple combinations of the first, second, and third harmonics. Terahertz emission has been reported using pump pulse durations >100 fs [17,18], and similar applications in the mid-IR region have exclusively used <100 fs pulses from Ti:S lasers [10]. Ultrafast broadband mid-IR sources generated using more cost-efficient and stable laser technologies would significantly expand the accessibility of newly developed mid-IR spectroscopies and microscopies.

In this Letter, we develop the first mid-IR source based on plasma generation in air pumped by a 171 fs, 1030 nm Yb:KGd(WO₄)₂ (Yb:KGW) femtosecond laser. This compact all-in-

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one system is a passively mode-locked, all-solid-state diode-pumped oscillator and amplifier [19]. Compared to a Ti:S laser, the Yb:KGW system offers better shot-to-shot stability and an adjustable repetition rate from 1 to 1000 kHz [20]. By focusing its first, second, and third harmonics in air, a plasma is generated that provides broadband, conical emission spanning from <1000 to 2700 cm^{-1} . The spectrum, mode, power, stability, and pulse duration are characterized. This source provides sufficient bandwidth to excite molecular vibrations in the mid-IR region for spectroscopy and microscopy, and retains the advantages of the stable and cost-efficient Yb:KGW laser system.

The design of the broadband infrared (BBIR) system extends the work of Petersen and Tokmakoff [12] to generate a mid-IR continuum by colinearly focusing the first, second, and third harmonics of an amplified femtosecond system in air (Fig. 1). A lens ($f = 100\text{ cm}$) is used to focus the amplified source (1030 nm, 171 fs, 1.7 mJ, 1 kHz divided down to 250 Hz, PHAROS, Altos Photonics) through four optical elements: type I β -barium borate (0.2 mm, $\theta = 23.4^\circ$, Altechna) for second-harmonic generation, a dual waveplate ($\lambda/2$ at 1030 nm + λ at 515 nm, Newlight Photonics Inc.), a rotatable calcite compensator (10–100 fs between 1030 nm(o) and 515 nm(e), AR at 1030/515 nm, Newlight Photonics), and type I β -barium borate (0.3 mm, $\theta = 32.5^\circ$, Altechna Co. Ltd.). The ionized air induced by the 1030 nm fundamental forms a plasma conversion media in which the three harmonics interact to produce broadband emission, although no filamentation was observed.

Entering the plasma, the pulse energies of the 1030/515/343 nm were 0.55/0.38/0.038 mJ. Conical IR emission is collimated by a 90° off-axis parabolic mirror (OAP) with a $\varnothing 2\text{ mm}$ hole in the center, through which the first, second, and third harmonics are spatially separated from the IR. A germanium window is used as a longpass filter to reject scattered light. We note that the optimal signal is generated when BBO1 is set for maximum conversion efficiency, and BBO2 is rotated -24° or $+27^\circ$ from normal in the azimuthal direction. A longer focal length for L1 (100 versus 75 cm) was found to increase the mid-IR output.

To characterize the BBIR pulse duration in a pump-probe experiment, it is spatially overlapped and delayed relative to a portion of the 1030 nm fundamental. Approximately 1% of the 1030 nm output is split off using the reflection from a microscope cover slip to form the pump beam. This passes through a delay line composed of a broadband retroreflector mounted on a linear positioner (SLC-1740, SmarAct GmbH) and focused by a lens through a 90° off-axis parabolic mirror with a centered $\varnothing 3\text{ mm}$ hole. The BBIR is made collinear and focused with the same 90° off-axis parabolic mirror, then recollimated and sent to the interferometer. An optical chopper (Thorlabs Inc.) blocks every other pump pulse for differential detection.

A home-built Michelson interferometer is used to characterize the BBIR spectrum. A CaF_2 beam splitter is used to separate the BBIR pulses into equal replicas that are retroreflected, recombined on the beam splitter, and focused onto a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. One retroreflector is mounted on a linear positioner (SLC-1740, SmarAct GmbH) to scan the interferometric delay. The delay is scanned, and the interference signal is collected using LabView software and field-programmable gate

array electronics (National Instruments). The spectrum is recovered by taking the absolute value of the Fourier-transformed interferogram. For pump-probe experiments, the pump-on and pump-off interferograms are saved separately.

Previously reported BBIR sources based on mixing the fundamental and second harmonic of a Ti:S laser have reported conical emission [15,16]. This arises from a mismatch in the confocal parameters at the pump and BBIR emission wavelengths [8]. To determine if this mode also appears in BBIR systems that combine the fundamental, second, and third harmonics, the mode was characterized by scanning a pinhole aperture across the BBIR. A 1 mm aperture was used to sample the beam after collimation to produce the data shown in Figs. 2A and 2C, which characterize the conical nature of the beam and its intensity asymmetry. The two lobes were 11.5 mm apart with full width at half-maxima of 1.3–1.6 mm. Despite a mode that appears to consist of higher-order combinations in a cylindrical beam expansion, it could be focused to approximately a Gaussian with 0.23 mm full width at half-maximum.

A zinc selenide wire grid polarizer was used to verify that the polarization of the BBIR radiation was linear (70:1 extinction), as previous measurements have reported [12,13,15,16] and parallel to the third harmonic. This beam mode analysis demonstrates the capability of the conical beam mode of the BBIR to be collimated and focused.

The spectral characterization of the BBIR shown in Fig. 3 reveals a bandwidth that peaks at 1300 cm^{-1} and spans from 1000 to 2700 cm^{-1} . The spectrum was obtained from 50 time-domain averages of a 16 ps interferogram with 1.5 fs steps. The bandwidth is limited by the sharp cutoff of the CaF_2 beam splitter at 1000 cm^{-1} and the gradual decrease in detector responsivity toward 3000 cm^{-1} . Based on the bandwidth observed from previous plasma sources, it is likely that the broadband emission extends into the far IR [10-13]. Residual water vapor and carbon dioxide lines are visible around 1600 cm^{-1} and at 2350 cm^{-1} after purging the system to 0.6% relative humidity at 23°C .

The spectrum in Fig. 3 was accompanied by changes in the spectra of the second and third harmonics emerging from the plasma, although these were not indicative of optimal alignment. The second harmonic was redshifted and broadened by $\sim 250\text{ cm}^{-1}$, as measured by the first moment and standard deviation. The third harmonic was blueshifted by $\sim 480\text{ cm}^{-1}$ and broadened by $\sim 1400\text{ cm}^{-1}$. No significant changes were observed in the fundamental ($<50\text{ cm}^{-1}$).

The intensity of the BBIR was measured as a function of the fundamental pulse energy (see Fig. 4). This power dependence represents a combination of the conversion efficiencies for the sum-frequency processes generating the second and third harmonics, as well as the processes generating the BBIR emission. Figure 4A shows that BBIR intensity increases sharply as the pump pulse energy is increased. The initial power dependence is consistent with a four-wave mixing process of the fundamental and second harmonic

($I_{BBIR} \propto |E_{1030}E_{1030}E_{515}|^2 = I_{1030}^4$). At higher pulse energies ($> 1.5\text{ mJ}$), where the third harmonic becomes non-negligible, the power dependence transitions to a $I_{BBIR} \propto I_{1030}^8$ functional form; this cannot be explained by four-wave mixing of all harmonics

($I_{BBIR} \propto |E_{1030}E_{515}E_{343}|^2 = I_{1030}^6$), and may arise from a sequential or parallel cascaded process [21]. This higher-order process also results in a blueshift of the spectrum as intensity $>1600 \text{ cm}^{-1}$ increases promptly about the 1.5 mJ transition (see Fig. 4B), which has previously been observed in BBIR generation with three harmonics [12].

The shot noise resulting from continuum generation processes is known to compound noise that appears in the pump and typically decreases with increasing pump pulse energy until the point of multiple filament generation [22]. The power dependence of the noise in this BBIR source is represented by the error bars in Fig. 4A. At maximum power, the plateau is 0.5%, which is below the fluctuations in some Ti:S amplifier outputs, and is among the lowest reported in a continuum BBIR source of this type (see Table 1). Stability of the BBIR arises from the low noise of the Yb:KGW laser [20], which was measured to be 0.2% RMS using an energy meter (QE8SP-B-BL, Gentec Electro Optics, Inc.) This energy meter was also used to calibrate our MCT detector to measure the total BBIR power produced. By comparing the relative detector sensitivities across the BBIR ($\sim 45\%$) and at 1030 nm ($\sim 10\%$), we measure a total BBIR output of 190 pJ.

The pulse width of the BBIR is measured by fitting the rise in transient reflectance of a 1 mm germanium sample pumped by the 1030 nm fundamental. A glass slide (see Fig. 1) splits a $\sim 1\%$ portion of 1030 nm light, which acts as the pump, and the BBIR acts as the probe. When germanium is excited above its bandgap (0.67 eV or $1.85 \mu\text{m}$), an electron-hole pair is generated that diminishes IR transmission with intra-band relaxation and thermalization occurring on 0.1–100 ps timescales [23]. This response is shown in Fig. 5, and was fit with a convolution model that considers the measured envelope for the 1030 nm pump (approximately Gaussian with $\tau_p^{1030 \text{ nm}} = 171 \text{ fs}$), a step response followed by relaxation for the germanium ($T_{\text{fast}} \approx 10 \text{ fs}$; $T_{\text{slow}} = 4.2 \text{ ps}$), and a Gaussian envelope for the BBIR probe ($\exp[-4 \ln(2)t^2/\tau_p^2]$). The extracted pulse duration of the BBIR ($\tau_p^{BBIR} 171 \pm 5 \text{ fs}$) was equal to that of the 1030 nm fundamental used to generate the BBIR. This pulse duration is similar to that observed in analogous sources producing filaments with shorter pulses from a Ti:S laser system [13]. The pulse duration expected from a transform-limited pulse with the amount of mid-IR bandwidth produced is 43 fs; in this Letter, no attempt was made to further compress the pulse.

We have demonstrated the generation of BBIR pulses by plasma generation in air driven by the fundamental, second, and third harmonics of an Yb:KGW laser. When driven by 171 fs pulses at 1030 nm, this system produced 190 pJ of BBIR with a bandwidth spanning <1000 to 2700 cm^{-1} , 171 fs pulse width, 0.5% RMS stability, and linear polarization. This Letter combines the stability and femtosecond pulse duration of the Yb:KGW source with a bandwidth across the mid-IR region necessary for broadband and ultrafast vibrational microscopies [2-4,24-26]. The conversion efficiency and bandwidth of this source may be further improved by using pressurized nitrogen or argon media [14-16] or by controlling the polarization of the third harmonic. The observed conical beam mode provides a straightforward means to combine the BBIR with other light sources, such as for pump-probe spectroscopy, and may be desirable for superresolution microscopy [27]. Further pulse

shaping may be used to obtain a mode suitable for diffraction-limited imaging or to further compress the pulse [28].

To investigate whether this source provides enough energy for our desired applications in single-molecule vibrational spectroscopy, we estimate the pulse energies required to excite a single vibrational transition. We consider direct IR excitation of a strong chromophore: the amide I vibration of a globular protein, bovine serum albumin [29], in the 1600–1700 cm^{-1} region (molar absorptivity $\epsilon \sim 3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ or absorption cross section $\sigma \sim 1 \times 10^{-15} \text{ cm}^2$). For a diffraction-limited spot formed using an NA = 0.65 microscope objective (spot area $A \sim 6 \times 10^{-7} \text{ cm}^2$), 1 in 6×10^8 photons (A/σ) would be absorbed. Therefore, the spectral energy density must be $\sim 20 \text{ pJ}$ in this 100 cm^{-1} region for one absorption event per pulse. Spectral integration demonstrates that the broadband IR source presented here, in addition to several others described in Table 1, provide sufficient energy for ~ 1 excitation event per laser shot in a strong vibrational chromophore.

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Fig. 1.

Broadband IR generation and characterization instrument layout. Abbreviations: Yb:KGW, femtosecond oscillator/amplifier (PHAROS, Altos Photonics); L1-2, UV fused-silica plano-convex lens ($f = 100$ cm and 25 cm); BBO1-2, type I β -barium borate; WP, 1030 nm/515 nm dual waveplate; CC, calcite compensator; OAP1-4, 90° off-axis parabolic mirror (RFL = 9", 4", 2", and 4") Ge, 1 mm Ge window, AR at 3–12 μm ; BB, beam block; CS, microscope cover slip; RR, broadband retroreflector mounted on linear positioner; CH, optical chopper; BS, 50% at 2–8 μm , 8 mm CaF_2 ; C, CaF_2 compensator; MCT, LN_2 -cooled HgCdTe detector.

Fig. 2. Spatial mode of the broadband IR. Contour plots of the intensity were characterized A: after collimation and B: at the focus. Y slices (at $x = 0$) and X slices (at $y = 0$) from A and B are shown in C and D.

Fig. 3. Broadband IR spectrum measured to 2 cm^{-1} resolution. The extent of the bandwidth to the low- and high-energy wings is limited by the calcium fluoride beam splitter transmission and mercury cadmium telluride detector response, respectively. The residual absorption from the water and carbon dioxide is evident at around 1600 and 2350 cm^{-1} , respectively.

Fig. 4.

Power dependence of the total broadband IR A: intensity and B: spectrum. The error bars depicted in A: represent the root mean square intensity, as characterized by 104 shots at 250 Hz. The spectra in B: were smoothed to a 30 cm^{-1} resolution to clarify the power-dependent trend.

Fig. 5. Transient reflectance of germanium in response to excitation at 1030 nm. A convolution model fit establishes a pulse duration of 171 fs for the BBIR.

Table 1

Review of Relevant Advancements in the Development of Broadband Mid-IR Sources Using Filamentation in Gas Media^a

Pump Characteristics		Plasma Medium	Emission Characteristics		RMS Stability	Conversion Efficiency	References		
800 nm	65 fs	150 μJ	Air	(17–267 cm ^{−1}) ^b	~5 pJ	240 fs	NR	~3 × 10 ^{−8}	[9]
800 nm	25 fs	1.8 mJ	Air	<1800–> 4000 cm ^{−1}	1.5 μJ	12.9 fs	5%	~8 × 10 ^{−4}	[10]
815 nm	50 fs	30 mJ	680 torr air	~3–2500 cm ^{−1}	5 μJ	NR	NR	1.7 × 10 ^{−4}	[11]
800 nm	35 fs	400 μJ	Air	<400–> 3300 cm ^{−1}	~10 nJ	100–150 fs	5%	~2.5 × 10 ^{−5}	[12]
800 nm	25 fs	1 mJ	Air	<400–> 5000 cm ^{−1}	NR	~150 fs	NR		[13]
800 nm	30 fs	3 mJ	909 torr Ar	1250–5000 cm ^{−1}	>0.4 μJ	sub-20 fs	<3.3%	>1.3 × 10 ^{−4}	[14]
800 nm	25 fs	0.9 mJ	Ar	500–5000 cm ^{−1}	250 nJ	7.4 fs	2.5%	2.8 × 10 ^{−4}	[15]
790 nm	30 fs	0.85 mJ	N ₂	400–5500 cm ^{−1}	~0.5 μJ	6.9 fs	1.6%	~6 × 10 ^{−4}	[16]
1030 nm	171 fs	1.7 mJ	Air	<1000–2700 cm ^{−1}	190 pJ	171 fs	0.5%	1.1 × 10 ^{−7}	This Letter

^aNR = Not reported.

^bIndicates estimated from reported bandwidth to 0.1% edges.