Ultrashort infrared 2.5–11 μm pulses: spatiotemporal profiles and absolute nonlinear response of air constituents

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We measure the detailed spatiotemporal profiles of femtosecond laser pulses in the infrared wavelength range of $\lambda = 2.5–11 \mu m$ and the absolute nonlinear response of major air constituents (N$_2$, O$_2$, and Ar) over this range. The spatiotemporal measurements reveal wavelength-dependent pulse front tilt and temporal stretching in the infrared pulses. © 2019 Optical Society of America

There is increasing development of intense short pulse laser sources from the mid-infrared (MIR) through the long-wave-infrared (LWIR) region. These include nonlinear optics-based sources such as optical parametric amplification (OPA) [1], difference frequency generation (DFG) [2], and optical parametric chirped pulse amplification (OPCPA) [3], as well as solid state gain media [4] and high pressure CO$_2$ gas lasers [5]. The existence of air transparency windows within the MIR–LWIR range [6] has motivated the study of their propagation in atmosphere and applications such as remote sensing in the molecular fingerprint region [7], high harmonic generation [8], and shaped multi-octave supercontinuum (SC) generation [9]. Important to all these applications is nonlinear propagation, which depends on the near-instantaneous (electronic) and delayed (rotational, vibrational) nonlinear responses of the medium. For the 50–300 fs MIR–LWIR pulses of this experiment, the electronic and rotational responses dominate; the non-resonant Raman vibrational response of O$_2$ and N$_2$ is negligible, owing to insufficient optical bandwidth.

In this Letter, we present measurements of the detailed spatiotemporal profiles of femtosecond laser pulses in the infrared wavelength range of $\lambda = 2.5–11 \mu m$ and the absolute nonlinear response of major air constituents (N$_2$, O$_2$, and Ar) over this range. We also investigate possible resonant two-photon vibrational excitation of N$_2$ near $\lambda = 8 \mu m$, which is of interest for high power LWIR laser pulse propagation [10]. The spatiotemporal measurements reveal the wavelength-dependent pulse front tilt and temporal stretching induced by the DFG scheme used to generate the infrared pulses.

There is a paucity of absolute nonlinear response measurements in the MIR and LWIR. Recent work includes measurements by our group of the nonlinear response of air constituents in the range of $\lambda = 0.4–2.4 \mu m$ [11] using single shot SC spectral interferometry (SSSI) [12–15], which enables separation of electronic and rotational contributions to the total nonlinearity. For $\lambda \sim 10 \mu m$ pulses, the total electronic plus rotational response of major air constituents and noble gases was measured [16,17] using four-wave mixing of two rotational lines from a 200 ps CO$_2$ laser pulse. In that case, the long pulsewidth and the time-integrated measurement prevented separation of the electronic and rotational contributions.

Here, we use SSSI to measure the space- and time-resolved nonlinear phase shift imparted on a weak SC probe pulse by the MIR–LWIR pump pulse-induced refractive index shift in the gases studied. As discussed in Ref. [11], the extracted nondegenerate nonlinearity coefficients are within ~5% of their degenerate MIR counterparts, with even better agreement in the LWIR. As depicted in Fig. 1, the MIR–LWIR pump at $\lambda_{DF}$ is generated by non-collinear DFG (Light Conversion) between ultrashort signal $\lambda_s = 1.1–1.6 \mu m$ and idler $\lambda_i = 1.6–2.6 \mu m$ pulses in a nonlinear crystal (AgGaS$_2$). The signal and idler were generated by an OPA (HE-TOPAS Prime, Light Conversion) pumped by 36 fs, 8 mJ pulses centered at $\lambda \sim 806 \text{ nm}$ from a 1 kHz Ti:sapphire amplifier system. SC pulses (400–750 nm) were generated from filamentation of ~200 μJ, 806 nm laser pulses from the same laser, focused at ~f/150 in a 2.5 atm xenon gas cell, followed by a Michelson interferometer, which splits the pulse into a SC reference–probe pair separated by ~2.5 ps. The SC pair co-propagates with the MIR-LWIR pump pulse into the gas target cell, with the reference pulse in advance of the pump and the probe overlapped with it and encoded with the pump-induced transient nonlinear phase shift. Polarization of the SC pulses is adjusted by rotating the polarization of the Ti:sapphire laser pulse entering the Xe cell with a $\lambda/2$ plate. Two gas pressure ranges were used in the target gas cell. For pump pulses $\lambda_{DF} = 3.0–6.5 \mu m$, the cell was filled to 1 atm with the test gases (N$_2$, O$_2$, and Ar). For pump pulses $\lambda_{DF} = 7.0–11.0 \mu m$, the cell was filled to 42 atm. This was done to increase the signal-to-noise ratio, as the output of the DFG...
drops to <10 μJ at λ = 11 μm. The pump focusing lens and entrance window of the gas cell are BaF2 to avoid absorption losses. The focal plane of the reference/probe in the cell interaction region is imaged onto the slit of an imaging spectrometer. The reference and probe interfere in the spectral domain, producing a two-dimensional (2D) spectral interferogram ΔΦ(ω, x) (space resolution x along the slit, spectral resolution ω perpendicular to the slit) at the spectrometer’s focal plane CCD camera. A chopper wheel blocks and unblocks the pump pulse on consecutive shots, enabling subtraction of pump-off background interferograms from pump-on shots. Pump–probe group velocity walk-off is negligible (<2 fs) in the gas targets of this experiment. In a procedure described previously [12], Fourier analysis of ΔΦ(ω, x), using the measured spectral phase of the probe, gives the one-dimensional (1D) space- and time-resolved phase shift Δφ(x, t) imposed on the probe by the pump-induced refractive index shift in the test gas. Time and space resolution in these measurements is ~5 fs and ~3 μm.

The refractive index shift Δφ(x, t) experienced by the probe is the sum of the electronic and rotational responses; if the phase shift imposed on a probe polarized parallel to the pump is Δφ∥(x, t) = Δφelc(x, t) + Δφrot(x, t) + Δφelc(x, t), then the phase shift imposed on a probe polarized perpendicular to the pump is Δφ⊥(x, t) = Δφelc(x, t)/3 − Δφrot(x, t)/2 [18]. Solving yields the pure electronic and rotational phase shifts in terms of the parallel and perpendicular phase shifts: Δφelc(x, t) = 3(Δφ∥(x, t) + 2Δφ⊥(x, t))/5 and Δφrot(x, t) = 2(Δφ∥(x, t) − 3Δφ⊥(x, t))/5.

In Figs. 2(a) and 2(b), we first show spatiotemporal traces of MIR–LWIR pulses using Ar as the test gas and parallel probe polarization. Here, the extracted phase shift imposed on the probe pulse is Δφ∥(x, t) = 2n2(λ, x, t)k∥L [15] from the near-instantaneous electronic nonlinearity of Ar (for a purely electronic nonlinearity, where k∥ = 2π/λ∥ is the probe central wavenumber, n2 is the nonlinear refractive index of electronic, and L is the interaction length, which cancels out in the analysis. The phase shift profiles are therefore a record of the spatiotemporal intensity profile |I(x, t)|. To the best of our knowledge, these are the first direct single shot measurements of spatiotemporal intensity profiles in the MIR–LWIR. It is seen that SSSI reveals pulse front tilt in the DFG-generated pulses, with the effective tilt angle decreasing with increasing λ. The traces also show pulse temporal broadening for increasing λ. The tilt is a consequence of phase matching in non-collinear DFG, and the broadening is dominated by strongly increasing group velocity dispersion (GVD) in our optical materials at long λDF.

For N2 test gas, Δφ∥ and Δφ⊥ imposed on the probe by a λ = 3.5 μm pump in N2 are shown in Figs. 2(c) and 2(d), and the extracted phase shifts are shown in Figs. 2(e) and 2(f). The negative Δφ⊥ in Fig. 2(d) occurs from perpendicular sampling of molecules whose ensemble average axis alignment is along the pump polarization, which gives a deficit in phase shift compared to the case of random alignment. Notable in Fig. 2 are the similar pulsewidths of the DFG-generated pulse front tilt in the DFG-generated pulses, with the effective tilt angle decreasing with increasing λ. The traces also show pulse temporal broadening for increasing λ. The tilt is a consequence of phase matching in non-collinear DFG, and the broadening is dominated by strongly increasing group velocity dispersion (GVD) in our optical materials at long λDF.

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the same pump wavelength they are equal to within measurement error). At \( \lambda = 6.5 \) \( \mu \)m, the FWHM is 92 fs. Extraction of the \( n_2 \) coefficients from \( \Delta \varphi_1 \) and \( \Delta \varphi_L \) proceeds as in our prior work \[11\], where we reference these measurements to the rotational responses in nitrogen and oxygen without explicit need for gas density, interaction length, or pump intensity profile measurements. The electronic and rotational phase shifts can be written as

\[
\Delta \varphi_{\text{elec}}(x,t) = 2n_2 I_0 k_p L(N/N_0) f(x,t),
\]

\[
\Delta \varphi_{\text{rot}}(x,t) = 2\pi N n_0^3 I_0 k_p L \Delta \alpha(\lambda_p) \Delta \alpha(\lambda_{pu}) g(t) * f(x,t), \tag{1}
\]

where \( n_2 \) and \( n_0 \) are the nonlinear (electronic) and linear refractive indices at 1 atm, \( I_0 \) is the peak spatiotemporal intensity, \( f(x,t) \) is the normalized intensity envelope, with peak value of one, \( N \) is the molecular density, \( N_0 \) is the molecular density at 1 atm, \( L \) is the interaction length in peak, \( \Delta \alpha(\lambda_p) \) and \( \Delta \alpha(\lambda_{pu}) \) are the rotational and electronic molecular polarizability anisotropy \[11,14\] at the probe and pump wavelengths, and the convolution \( I_0 \Delta \alpha(\lambda_{pu}) g(t) * f(x,t) = I_0 \Delta \alpha(\lambda_{pu}) \int_{-\infty}^{\infty} g(t-t') f(x,t') dt' \) is the ensemble average transient alignment induced by the pump pulse. In the latter expression, we use the rescaled impulse response function for quantized rotations of a rigid molecular rotor \[14,15\],

\[
g(t) = \frac{(-1)^{j+1}}{\gamma \Gamma(\gamma)} \sum_{\pm \gamma} r_{\pm \gamma} e^{-\gamma t} \sin \omega_{j, \delta} t,
\]

where the thermal population of rotational state \( j \), \( \omega_{j, \delta} t \), is the transition frequency and depolarizing rate between states \( j \) and \( \delta \), and \( B \) is the rotational constant of the molecule.

Expressed directly as a refractive index shift experienced by the probe pulse, \( \Delta \varphi_{\text{elec}}(x,t) = 2n_2 I_0 (x,t) + \int_{-\infty}^{\infty} R(t-t') f(x,t') dt' \), where the impulse response function is \( R(t) = 2\pi N n_0^3 \times \Delta \alpha(\lambda_p) \Delta \alpha(\lambda_{pu}) g(t) \). It is clearly seen from the expressions in Eq. (1) how \( n_2 \) is extracted given the measured 2D datasets \( \Delta \varphi_{\text{elec}}(x,t) \) and \( \Delta \varphi_{\text{rot}}(x,t) \), the measured 2D spatiotemporal envelope \( f(x,t) \) (from the electronic response), and the known impulse response \( g(t) \), with \( N, I_0 \) and \( L \) cancelling out. For nitrogen, the dispersion in \( \Delta \alpha \) is even weaker in the MIR–LWIR than in our prior case at \( \lambda < 2.4 \) \( \mu \)m \[20,21\], with \( \Delta \alpha_N(\lambda_{pu}) \approx \Delta \alpha_N(0) = 6.6 \times 10^{-25} \) \( \text{cm}^3 \) \[11\]. For oxygen, we assume \( \Delta \alpha(O_2) \approx \Delta \alpha(\lambda_{pu}) \) for all analyses, and we use the values of \( \Delta \alpha(\lambda_{pu}) = 10.2 \times 10^{-25} \) \( \text{cm}^3 \) measured in Ref. \[15\].

For each molecular dataset, the analysis proceeds in practice by performing the 2D least squares fit \( g(t) \times \Delta \varphi_{\text{elec}}(x,t) = \mu_1 \Delta \varphi_{\text{elec}}(x,t) \) to yield \( \mu_1 \), where \( \Delta \varphi_{\text{elec}} \) and \( \Delta \varphi_{\text{rot}} \) are the 2D SSSI traces. Each SSSI trace has \( n \approx 100 \) points in \( x \) and \( n \approx 50–100 \) points in \( t \), enabling <10^4 points for fitting per shot. This gives the best fit value of \( n_2 = \mu_1 N n_0^3 / N_0 \Delta \alpha(\lambda_p) \Delta \alpha(\lambda_{pu}) = \mu_1 N n_0^3 / N_0 \Delta \alpha(\lambda_{pu}) \). Here, as discussed, \( \Delta \alpha(\lambda_{pu}) \) is taken as spectrally flat, and the Kerr coefficient \( n_2 \) of Ar is measured relative to that of nitrogen using the same pump pulse parameters. Performing a 2D least squares fit \( g(t) \times \Delta \varphi_{\text{elec}}(x,t) = \mu_2 \Delta \varphi_{\text{elec}}(x,t) \) gives \( n_2 = \mu_2 N n_0^3 / N_0 \), from Eq. (1).

At the longer wavelengths produced by the DFG, the conversion efficiency drops due to the Manley–Rowe relations. In order to maintain the signal-to-noise ratio at an acceptable level for pump wavelengths of >6.5 \( \mu \)m, we increased the test gas pressure to 42 atm. At higher pressures, colliional dephasing causes the rotational response function to decay exponentially with time, as seen in the expression for \( g(t) \). If we assume a dephasing rate \( \gamma_{j, \delta} \) independent of transition, then we can exploit the exponential decay of the peaks of the rotational revivals to extract \( \gamma \) by fitting \( \Delta \varphi_{\text{rot}}(x,t) \), to the full and half revivals measured near \( t = mT \) and \( t = (m + \frac{1}{2})T \) for \( m = 0–4 \), where \( T = (2eB)^{-1} = 11.6 \) ps is the revival period for \( \text{O}_2 \) \[14\]. Figure 3 shows the initial \( \Delta \varphi_{\text{rot}} \) response near \( t = 0T \) at \( 0T \) gas pressures of 1–4 atm, with all peaks normalized to one, followed by the revivals near \( t = \frac{1}{2}T \) and \( t = T \). The dashed line shows a decaying exponential fit to the revival curve for 8 atm. Extracting \( \gamma \) as a function of pressure yields the damping rate of \( \gamma = 5.4 \times 10^{0}(\text{s} \cdot \text{atm})^{-1} \). The rotational revival period for \( \text{O}_2 \) is \( T = 11.6 \) ps.
Table 1. Measured Values of $n_2 (\times 10^{-20} \text{ cm}^2/\text{W})$ (Electronic) for Major Air Constituents at Atmospheric Pressure

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<th>$\lambda$ (µm)</th>
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<tr>
<td>$3.0$</td>
<td>$0.67$</td>
<td>$0.77$</td>
<td>$0.76$</td>
<td>$0.74$</td>
<td>$0.72$</td>
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<td>$3.5$</td>
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<td>$0.85$</td>
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<tr>
<td>$4.0$</td>
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<td>$0.78$</td>
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<td>$5.0$</td>
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-negligible effect on the rotational response during the temporal window, where $\Delta \varphi_{\text{dc}}$ and $\Delta \varphi_{\text{ac}}$ are measured.

The results of our measurements and analysis are shown in Table 1. As in our prior results at $\lambda \leq 2.4$ µm in the MIR [11], there is little dispersion in $n_2$. In the region near $\lambda = 8.0$ µm for $N_2$, which was scanned continuously through 7.5–8.5 µm, we observed no signature of two-photon resonant absorption [10].

Spatiotemporal traces for pump pulses of $\lambda = 7–11$ µm are shown in Fig. 4. As in Fig. 2, all pulses generated by non-collinear DFG show a pulse front tilt. This is a natural consequence of the phase matching condition $k_S = k_I + k_{DF}$ and $k_S/n_2 = k_I/n_1 + k_{DF}/n_{DF}$, where $k_S$, $k_I$, and $k_{DF}$ are the signal, idler, and difference wavevectors; $k_S$, $k_I$, and $k_{DF}$ are their magnitudes; and $n_2$, $n_1$, and $n_{DF}$ are the refractive indices of GaAs, at those wavelengths, whose Sellmeier curves are found in Ref. [22]. In non-collinear geometry, the output pulse front tilt results from the intersection volume of the signal and idler shifting in time as they propagate through the non-linear crystal. Computing the tilt angle $\gamma$ as measured in the gas target, $\gamma = -M(k_{DF}/n_{DF})\beta/\delta k_{DF}$ [23], where $\beta$ is the angle of $k_{DF}$ from the crystal surface normal, and $M = 45$ is the pump lens demagnification factor, yielding $\gamma = 7.5^\circ$ at $\lambda = 3.0$ µm and $\gamma = 2.2^\circ$ at $\lambda = 6.5$ µm, in very good agreement with the tilt measurements with Figs. 2(a) and 2(b).

For small $k_{DF} = |k_S - k_I|$ (or long $\lambda_{DF}$), the crossing angle $\alpha$ between $k_S$ and $k_I$ is small, as is $k_S - k_I \approx k_{DF}$, so that the pulse front tilt is reduced at long $\lambda_{DF}$. However, temporal pulse stretching is enhanced at long $\lambda_{DF}$, owing to the increasingly negative GVDF($\lambda_{DF}$) [24] in the BaF$_2$ focusing lens and gas cell entrance window. The calculation of Fig. 4(b) shows the onset of strong broadening for $\lambda_{DF} \gtrsim 7$ µm, in agreement with the measurements of Fig. 4(a).

In conclusion, we have measured the electronic nonlinear index $n_2$ of the major air constituents Ar, O$_2$, and N$_2$ in the MIR--LWIR range of $\lambda = 2.5–11$ µm and presented spatiotemporal profiles of these pulses. The values of $n_2$ show no dispersion to within our measurement precision. We observe directly, for the first time, to the best of our knowledge, the pulse front tilt and temporal broadening produced by DFG and dispersion of femtosecond infrared laser pulses.


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REFERENCES AND NOTES

19. The expression for $g(t)$ in Ref. [11] is incorrect. This did not affect the results in that Letter, as numerical computations used the correct formula shown here.