

Supplemental Material for
Optical resonance imaging:
An optical analog to MRI with
sub-diffraction-limited capabilities

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1 The ORI Third-Order Response Function

The macroscopic polarization, $P(t)$, generated by an incident electric field connects a measured optical signal to the microscopic response of the molecules or materials. In the dipole approximation, this polarization can be expressed as

$$P(t) = Tr(\hat{\mu}\rho(t)) = \langle \hat{\mu}\rho(t) \rangle,$$

where $\hat{\mu}$ is the dipole operator, $\rho(t)$ is the time-dependent density matrix, and the angle brackets denote a trace.¹ In the perturbative regime where the electric field of the light only weakly couples to the material system, it is possible to perturbatively expand the density matrix. For a third-order nonlinear experiment, involving three interactions of an electric field with a sample at distinct

times denoted as t_1, t_2 , and t_3 , in the interaction picture, we can write the trace above as the following convolution integral

$$P^{(3)}(t) = \int_{-\infty}^t dt_3 \int_{-\infty}^{t_3} dt_2 \int_{-\infty}^{t_2} dt_1 E(t_1)E(t_2)E(t_3) \cdot R^{(3)}(t_1, t_2, t_3),$$

where E denotes an electric field interaction and $R(t_1, t_2, t_3)$ is a third-order response function that can be written

$$R^{(3)}(t_1, t_2, t_3) = \left(\frac{-i}{\hbar}\right)^3 \Theta(t_1)\Theta(t_2)\Theta(t_3) \langle \mu(t) \cdot [\mu(t_3), [\mu(t_2), [\mu(t_1), \rho(-\infty)]]] \rangle,$$

where $\Theta(t)$ is the Heaviside step function.

The time variables discussed above are defined for absolute times, but it is more useful experimentally to discuss time intervals corresponding to the time differences between a pair of pulses. As such we can make the following definitions:

$$t_1 = 0$$

$$\tau = t_2 - t_1$$

$$T = t_3 - t_2$$

$$t_R = t - t_3,$$

where τ is the time between pulses 1 and 2, T is the time between pulses 2 and 3, and t_R is the time between pulse 3 and the signal time t . This allows us to redefine the response function as $R^{(3)}(\tau, T, t_R)$.

In a canonical third-order nonlinear spectroscopic measurement, such as 2DES or 2DIR, where none of the pulses have pulse-front tilt, the third-order polarization generated in the sample, and thus the emitted third-order signal, is a function of three temporal intervals defined above. These three variables are controlled experimentally by moving an opto-mechanical delay line to delay one pulse's arrival relative to the other. Performing different measurements with different

values of τ and then Fourier transforming over this coordinate produces a frequency axis that is equivalent to spectrally resolving the pump frequency (or excitation frequency, ω_τ). The second time variable, T , corresponds to the time difference between pulses 2 and 3. During this time, the measured system is generally thought to be in a population state, meaning the system evolves in time as an eigenstate of the unperturbed Hamiltonian. Again, this time is controllable by varying the arrival time of pulse 3 relative to pulse 2 using an opto-mechanical delay line. The final time domain, t_R , is defined as the time after the third pulse, when the signal is emitted. This time domain is typically measured interferometrically by using a spectrometer to convert from time to frequency and mixing the signal with the local oscillator, producing the second frequency axis, or probe frequency, ω_{t_R} , presented in a typical 2D plot.

A nonseparable spatio-temporal coupling, such as pulse-front tilt, of pulse 3 means that arrival time of this pulse, ie. time variable t_3 , will vary across the sample as a function of position, allowing us to write the spatially-dependent temporal interval between pulses two and three as

$$t_3 - t_2 = T - px,$$

where p denotes pulse-front tilt and x is a spatial coordinate. As such the spatial-temporal coupling is present in the response function, which can be written as $R^{(3)}(\tau, T - px, t_R)$. Thus, all the time intervals, including T , remain experimentally controllable variables. This should enable the extraction of both two-dimensional spectra as well as optical resonant images from the same experimental setup, as long as all the time intervals are experimentally scanned.

2 Kostenbauder Matrix Calculations

The Kostenbauder formalism discussed in the main text allows us to follow the spatio-temporal coupling of pulse 3.² Fig. S1 confirms that the pulse still has a 15 fs FWHM.

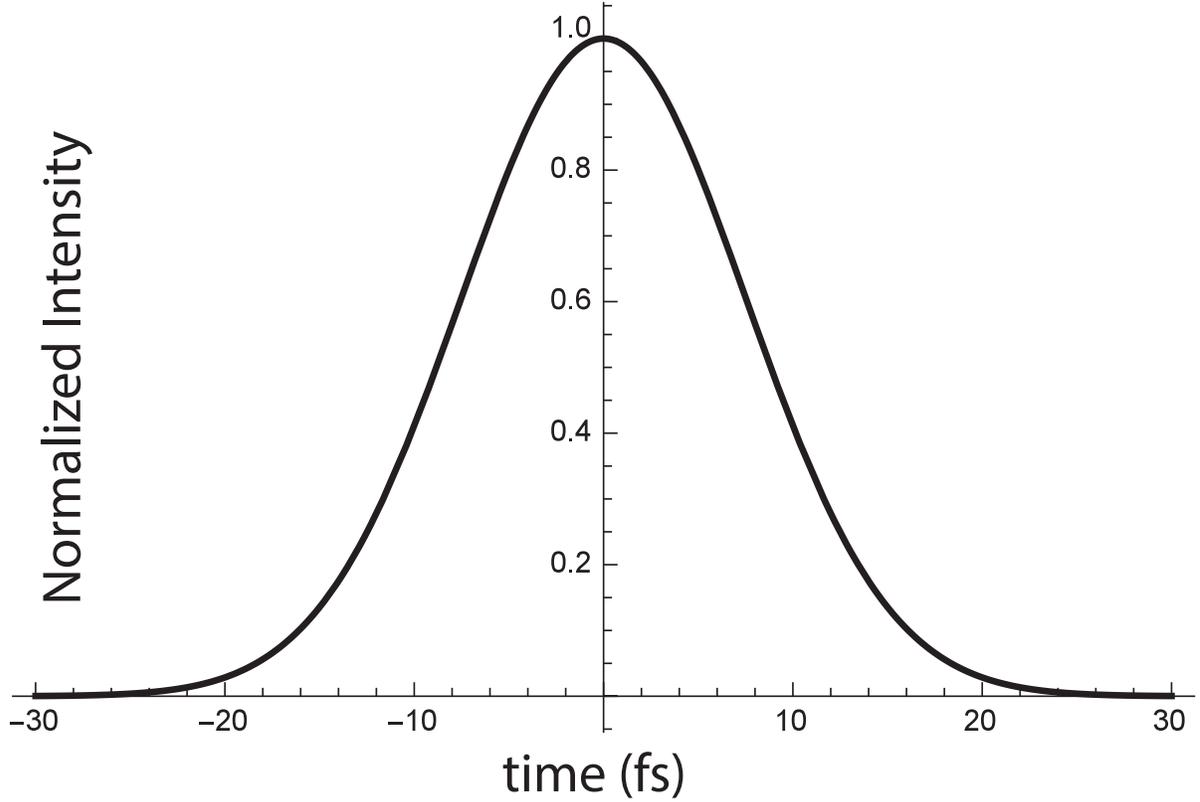


Figure S1. A slice through the point $x' = 0$ from Fig.1. The ordinate is in normalized intensity units.

3 Fourier Optics Simulation

The simulated ORI signal was calculated by propagating the emitted dipole fields through a $f/2$ optical system. Fig. S2 shows the field as calculated before the first lens. The lens applies a quadratic phase which cancels the phase from the emitted signal wave since the source was at the focus. The wave was then propagated to just before the second lens. The calculated collimated field can be seen in Fig. S3. Finally the field was propagated to the focus of the second lens, which in this model corresponds with the entrance slit of the simulated spectrometer. This simulated signal can be seen in Fig. S4.

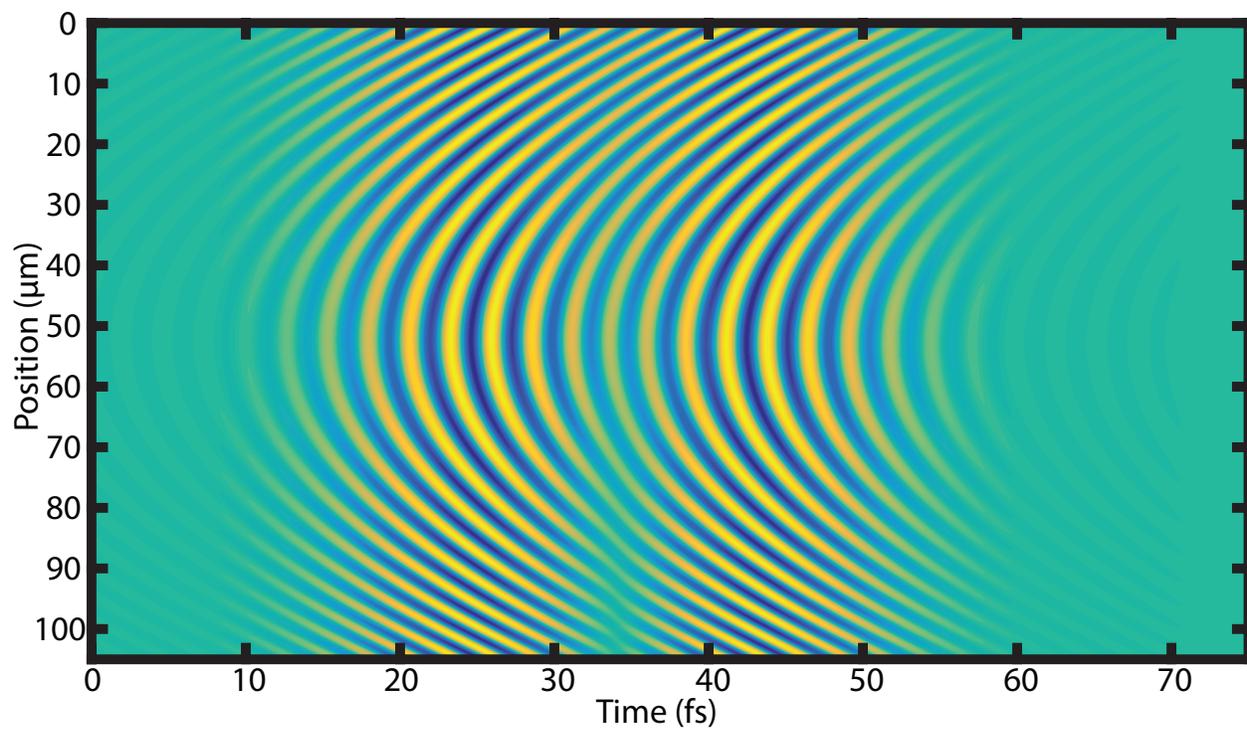


Figure S2. The real-valued electric field before the first lens of the collection optics.

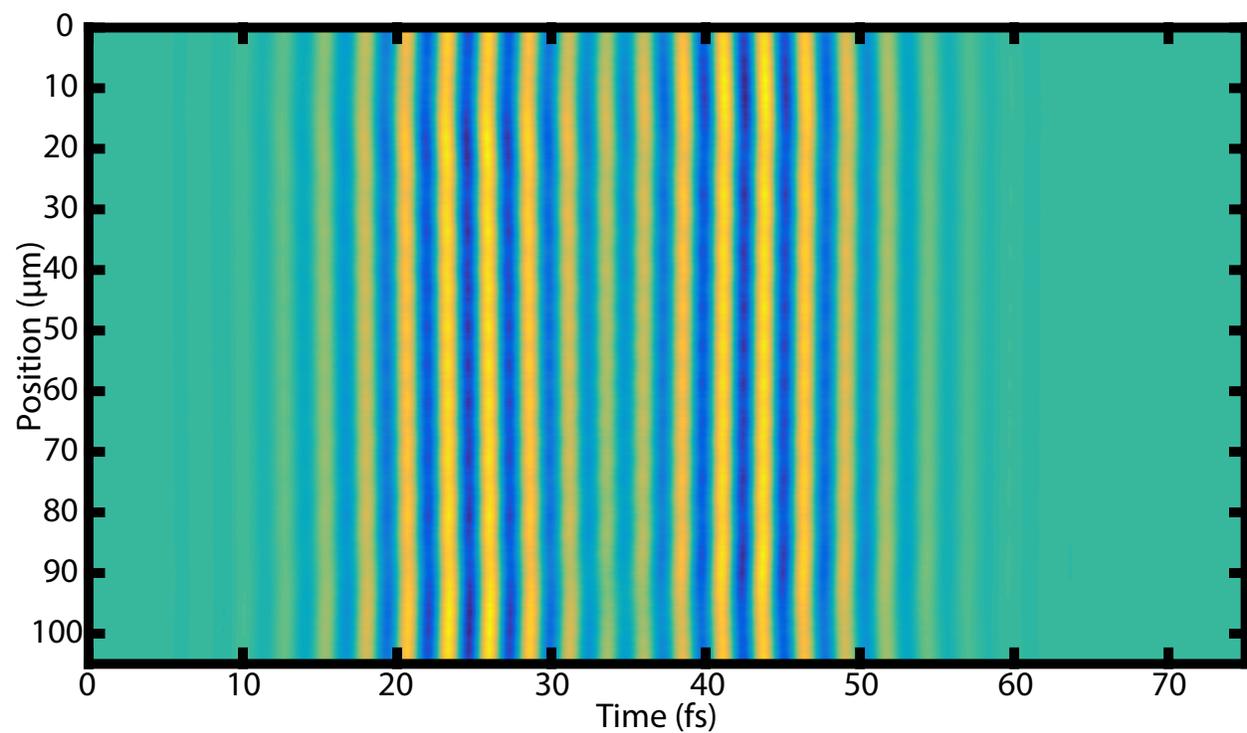


Figure S3. The real-valued electric field before the second lens of the collection optics.

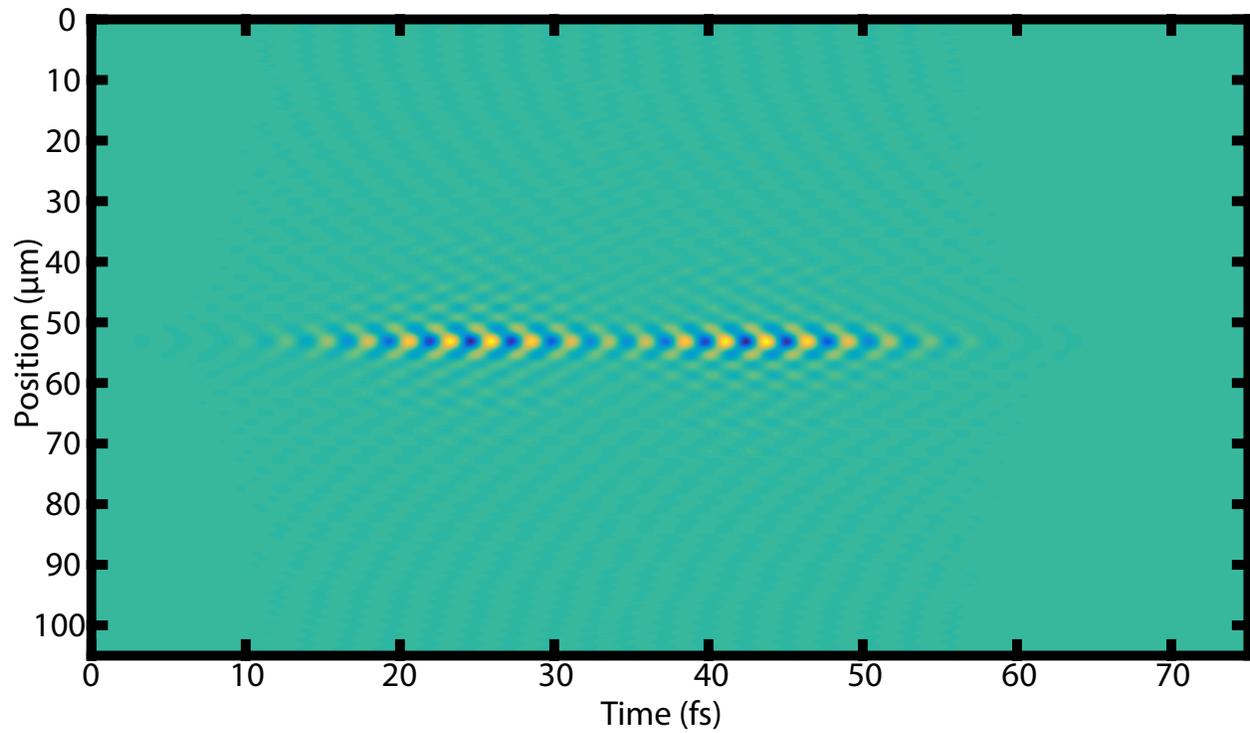


Figure S4. The real-valued electric field at the entrance slit of the simulated spectrometer.

References

- (1) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press, 1995.
- (2) Kostenbauder, A. Ray-pulse matrices: a rational treatment for dispersive optical systems. *IEEE J. Quant. Electron.* **1990**, *26*, 1148–1157.